Catalytic Chain Transfer Polymerization of Methacrylates and Styrene

by

Bashir Adamu

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

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In Partial Fulfillment of the
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In

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DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Bashir Adamu** under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE in Chemistry.

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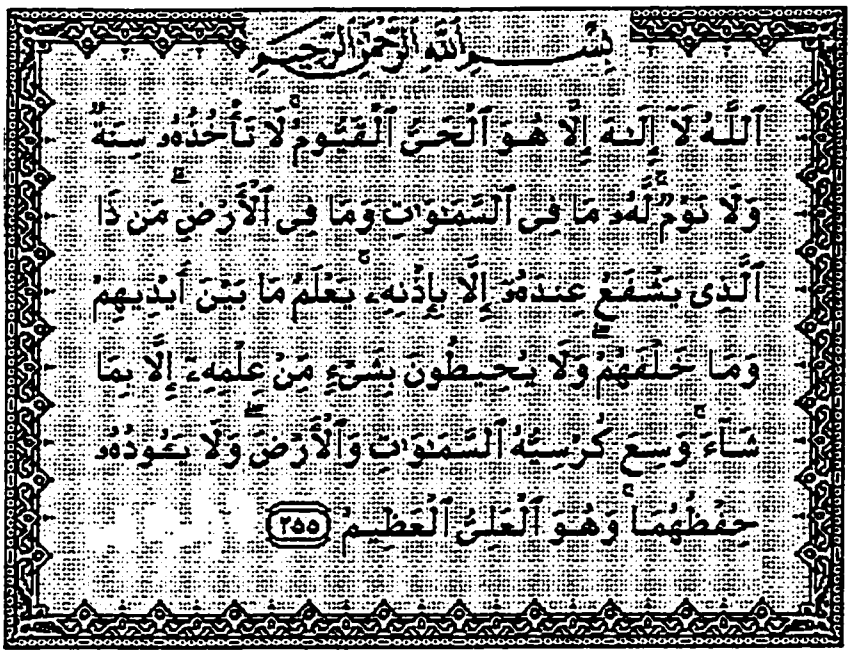
بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ
اللَّهُ لَا إِلَٰهَ إِلَّا هُوَ الْحَيُّ الْقَيُّومُ ۚ لَا تَأْخُذُهُ سِنَةٌ
وَلَا نَوْمٌ ۚ لَّهُ مَا فِي السَّمَاوَاتِ وَمَا فِي الْأَرْضِ ۗ مَن ذَا
الَّذِي يَشْفَعُ عِندَهُ إِلَّا بِإِذْنِهِ ۚ يَعْلَمُ مَا بَيْنَ أَيْدِيهِمْ
وَمَا خَلْفَهُمْ ۖ وَلَا يُحِيطُونَ بِشَيْءٍ مِّنْ عِلْمِهِ إِلَّا بِمَا
شَاءَ ۚ وَسِعَ كُرْسِيُّهُ السَّمَاوَاتِ وَالْأَرْضَ ۖ وَلَا يَئُودُهُ
حِفْظُهُمَا ۚ وَهُوَ الْعَلِيُّ الْعَظِيمُ ﴿٢٥٥﴾

Allâh! Lâ ilâha illa Huwa (none has the right to be worshipped but He), the Ever Living, the One Who sustains and protects all that exists. Neither slumber, nor sleep overtake Him. To Him belongs whatever is in the heavens and whatever is on earth. Who is he that can intercede with Him except with His Permission? He knows what happens to them (His creatures) in this world, and what will happen to them in the Hereafter . And they will never compass anything of His Knowledge except that which He wills. His Kursî[1] extends over the heavens and the earth, and He feels no fatigue in guarding and preserving them. And He is the Most High, the Most Great. [This Verse 2:255 is called Ayat-ul-Kursî.]

Dedicated to:

My parents, Brothers and Sisters

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ABSTRACT

Low molecular weight poly(acrylates and methacrylates) are extensively used as macromonomers in the syntheses of block and graft copolymers, and in the formulation of "high solids" paints and coatings. Molecular weight control is commonly achieved by using thiols. However, thiols impart undesirable properties such as color, odor and toxicity to the finished products. More recently, the use of cobalt (II) oximes has proved to be efficient in achieving molecular weight control. This new class of compounds works at parts per million levels. It also eliminates the problems encountered with conventional molecular weight regulators. This study involved the synthesis and characterization of cobalt alphafurildioxime $\{Co(\alpha\text{-fdo-}2H)_2(BF_2)_2.2H_2O\}$, and its use as a potential catalytic chain transfer agent (CCTA) in the bulk free radical homo- and co-polymerization of some methacrylates and styrene monomers. Azobis(isobutyronitile), AIBN was used as initiator. Elemental analysis and UV-visible technique were used to characterize the CCTA. Molecular weight of the resulting polymers was studied by dilute solution viscometry (DSV) and gel permeation chromatography (GPC). Catalytic chain transfer constant (C_S) values were evaluated using the Mayo equation. The effects of the chain transfer agent on polydispersity index (PDI) and monomer conversion were also investigated. Molecular weights obtained from both DSV and GPC and were found to decrease with increasing concentration of the CCTA. C_S values evaluated were comparable in magnitude to those reported in the literature. The samples had a relatively narrow polydispersity in the range of 1.5 to 2.0. Monomer conversion was found to decrease with increasing concentration of the CCTA. This has been attributed to retardation in rate of certain processes.

ملخص الرسالة

تستخدم مبلمرات البولي أكريليت والبولي ميثاكريليت ذات الوزن الجزيئي المنخفض بشكل واسع كمونومرات كبيرة الحجم في تحضير المبلمرات المشتركة المجمعة والمطعّمة، وكذلك في صياغة مواد طلاء " عالية الصلابة ". عادة يمكن التحكم بالوزن الجزيئي باستخدام الثيولات ، غير أن الثيولات تعطي خواص غير مرغوب فيها (مثل اللون ، الرائحة، السّمّية) للمنتجات النهائية ، وقد تم حديثاً استخدام أوكزيمات الكوبالت الثنائي حيث وجد أنها ذات فعالية للتحكم بالوزن الجزيئي وهي تعمل عند مستوى الجزء بالمليون. كما أنها تحد من المشاكل الناجمة عن منظمات الوزن الجزيئي التقليدية.

هذا البحث يتضمن تحضير ودراسة خواص مركب [كوبالت ألفا فيوريل دايوكزيم] $[Co(\alpha\text{-fdo-2H})_2(BF_2)_2\,2H_2O]$ ، وأهمية هذا المركب تكمن في إمكانية إستخدامه كعامل محفز للإنتقال إلى السلسلة (CCTA) في بلمرة الجذر الحر المجمعة المتجانسة و المشتركة لبعض مونومرات الميثاكريليت والستايرين باستخدام [آزوثنائي (أيزوبيوتيرونيتريل)] (AIBN) كبادئ للتفاعل.

لدراسة خواص CCTA تم استخدام تقنيتي التحليل الذري ومطيافية الأشعة فوق البنفسجية. أما الوزن الجزيئي للمبلمرات الناتجة فقد تم دراستها باستخدام مقياس درجة اللزوجة للمحلول المخفف (DSV) و تقنية كروماتوجرافيا النفوذ الهلامي (GPC) . كما تم تقدير قيم ثابت الإنتقال للسلسلة (Cs) باستخدام معادلة مايو وكذلك رصد تأثير عامل الإنتقال للسلسلة على دليل التشتت المتعدد (PDI) وعلى مقدار تحول المونومر. أيضا قدر الوزن الجزيئي بواسطة كلا من DSV و GPC ووجد أنه يتناقص مع زيادة تركيز CCTA . ووجد كذلك أن قيم Cs المقدرة يمكن مقارنة مقاديرها بالنسبة لما ذكر في الأدبيات. نتائج عينات الإختبار وجد أنها تملك مدى ضيق نسبيا من التشتت المتعدد (من ١،٥-٢) . أما بالنسبة إلى مقدار التحول للمونومر فقد وجد أنه يتناقص بزيادة تركيز CCTA ، ويمكن إرجاع ذلك إلى التناقص في معدل بعض عمليات البلمرة.

CHAPTER ONE

INTRODUCTION

1.1 Background

The polymerization of acrylic-based monomers does not usually involve transition metal complexes, except as redox couples for the regeneration of odd electron species. Molecular weight control in free radical-initiated systems is usually achieved by adjusting the initiator to monomer ratio or by addition of a transfer agent such as a thiol or mercaptan, to terminate the growing chains. For example, phenyl mercaptan is used as a chain transfer agent in the polymerization of MMA initiated by AIBN or Vazo-57 [1]. However, high concentrations of thiols and mercaptans and/or initiator are needed to achieve very low molecular weights. The use of such high amounts is associated with problems such as cost, toxicity, color and odor in the resulting products.

Cobalt(II) complexes of tetra-aza-ligands such as porphyrins [2] or dimethylglyoximates [3-8] have proved to be extremely efficient catalysts in intercepting growing polymer chains. This activity is attributed to the radical nature of the cobalt(II) center in such complexes. A schematic representation of the mechanism by which they operate is shown in section 1.1.2. The rate at which

they intercept the growing chains is controlled by diffusion. Therefore, the larger the surface area of the complex, the less efficient it will be as a chain transfer agent. For this reason, catalytic chain transfer studies are conducted at low monomer conversion, in order to eliminate the influence of viscosity on the diffusion of the transfer agent molecules to the chain ends.

Molecular weights have been shown to drop from hundreds of thousands down to thousands, upon addition of parts per million concentrations of these complexes [1, 6]. Macromonomers incorporating just a few units of MMA have been synthesized at higher concentrations of these catalysts [9-12]. Interestingly, these macromonomers do not homopolymerize with each other, but copolymerize with other monomers to give graft, random and block copolymers having a wide range of applications [9, 11, 13-14].

In addition to this, low molecular weight polymers are used in the formulation of "high solids" automotive finishes, adhesives, acrylic-based paints, sprays and other related applications. For example, for metal-coating lacquers, poly(methyl methacrylate) of molecular weight range between 80,000 – 150,000 is required. Mechanical properties of acrylates and methacrylates, such as adhesion in paints and adhesives, are very much dependent on molecular weight [1, 15].

1.1.1 Chain Transfer Phenomena

In many polymerization systems, the observed molecular weight of the polymer is lower than that predicted on the basis of experimentally observed extents of termination by coupling and disproportionation. This arises as a result of premature termination of a growing polymer chain by the transfer of a hydrogen atom or other species to it from compounds like monomer, initiator, solvent, impurity or a chain transfer agent, etc [15-16] present in the system. The process by which the radical is removed from the growing polymer chain is called a chain transfer reaction, and the substances responsible for this are called "chain transfer agents", CTAs. These reactions can generally be represented by equation (1) below.

$$M_n \cdot + XA \xrightarrow{k_{tr}} M_n\text{—}X + A^{\cdot} \qquad (1)$$

where ($M_n^{\cdot}$ is a growing polymer chain, and XA may be any of the substances discussed above). Chain transfer is essentially a chain breaking reaction resulting in a decrease in the size of the propagating polymer chain. Chain transfer is important because it affects the molecular weight of the polymeric product formed. If controlled, it can be used to control of molecular weights to desirable lengths or limits [16].

Chain transfer to monomer is usually not very important, particularly in the case of monomers to be studied in this work. For example, the chain transfer constants for methyl methacrylate and styrene are 0.07-0.25 x 10^{-4} and 0.3-0.6 x $^{-10-4}$ respectively [16]. Thus, a study of chain transfer catalysis can be conducted without incorporating any serious error from monomer contribution. Table A1 (Appendix A) shows a list of monomers and their chain transfer constant (C_M) values. The choice of the proper initiator is important in the study of chain transfer catalysis, because initiator contribution to chain transfer may generally be substantial. Table A2 (Appendix A) shows chain transfer constant (C_I) values for some common free radical initiators

Chain transfer to solvent may however be important in the choice of solvents for a given polymerization reaction. In order to study the chain transfer potentials of a compound, it is necessary to prevent all other forms of chain transfer from occurring. This is usually achieved by working with highly pure monomers and initiators, in the absence of oxygen and solvent (bulk polymerization).

In general, chain transfer reactions of the type discussed and represented by equation (1) above proceed without regeneration of the transfer agent [2]. It is this factor that limits the practical utilization of high-efficiency chain transfer agents for the control of molecular weight distribution (MWD) of polymer, since they are totally consumed before full conversion of monomer is attained. The first indication of possible regeneration of chain transfer agent dates back to 1953 [2].

However, not much work was done in the area for a very long time. It is obvious that the catalysis of chain transfer offers several advantages over other methods of controlling the molecular weight distribution.

1.1.2 Mechanism of Catalytic Chain Transfer

The pioneering work of Enikolopyan *et al* [2] and the subsequent discovery of more efficient chain transfer agents have stimulated tremendous interest towards understanding the mechanism and kinetics of the catalytic chain transfer process. Earlier mechanistic studies were carried out using low spin Co(II) complexes of tetraarylporphyrins (TAP) [2]. More recently, a generalized mechanism for polymerization of MMA by low spin Co(II) complexes has been proposed, using BF_2-bridged cobalt dimethylglyoxime [3]. It is important to note that these substances do not initiate polymerization on their own [2]. Their presence in trace amount leads to a dramatic decrease in the molecular weight of the resulting polymer [2, 17-18], once polymerization is initiated using an initiator, for example AIBN. This generally accepted mechanism of catalytic chain transfer is shown in Figure 1.1 [17]. It was proposed on the basis of the observation that the oligomeric products obtained in the presence of a chain transfer agent bear a terminal double bond. Also, more polymer chains were formed than would be expected based on initiator concentration and efficiency. The origin of this unsaturation can only be explained satisfactorily by the mechanistic cycle shown in Figure 1.1 below.

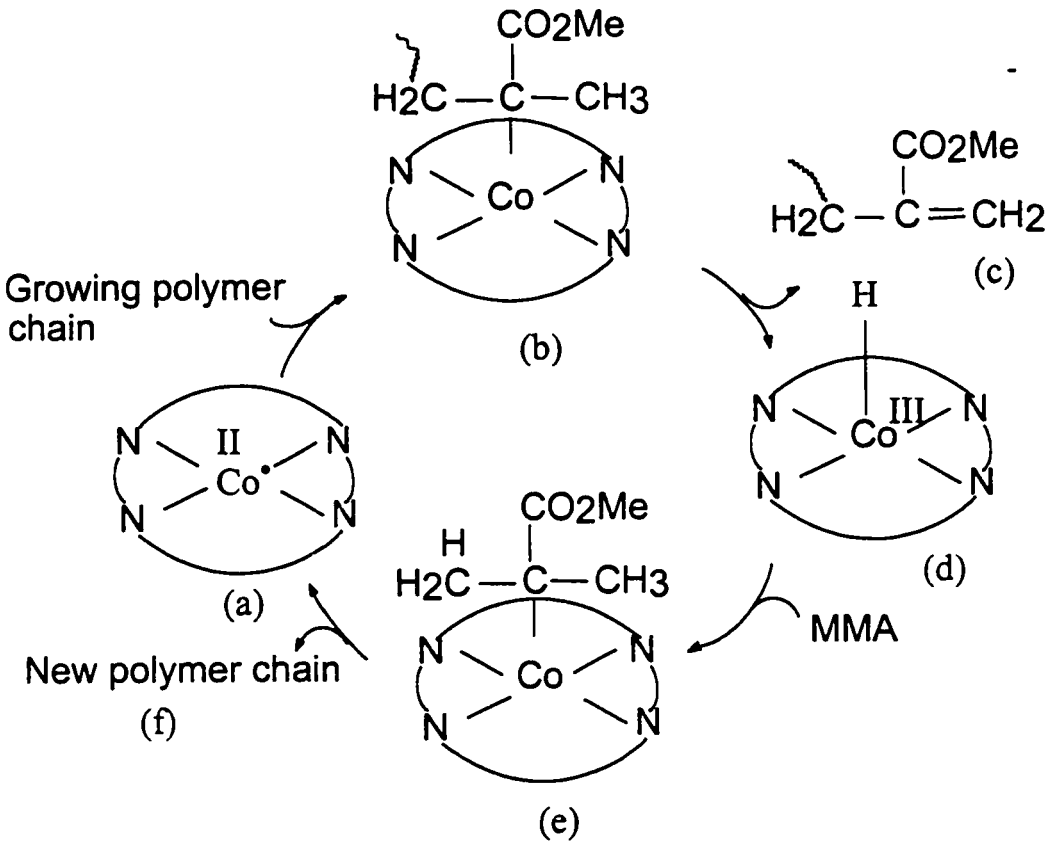


Figure 1.1 Tollman's Representation of the Catalytic Chain Transfer Mechanism [17].

The radical-like species labeled 'a' in the above figure, is generated in situ under the reaction conditions [3, 9]. The planar structure of the complex and the radical-like nature of the Co(II) ion, provide a favorable environment for interaction with a growing polymer chain as shown in 'b'. This interaction results in the oxidation of the Co(II) to Co(III) and formation of a labile Co — C bond. A β-hydride transfer from the adjacent methyl group to cobalt then occurs. This confers a

terminal double bond onto the terminated polymer chain 'c' and the Cobalt — hydride complex 'd' is formed. This hydride then reacts with another monomer molecule thereby initiating polymerization via hydrogen atom transfer, giving 'e', which grows into a propagating polymer chain 'f' by addition of more monomer, while the active Co(II) radical-like species 'a' is regenerated and the cycle continues.

The entire process of chain transfer as described above occurs at a diffusion-controlled rate. Consequently, all kinetic and mechanistic studies on chain transfer processes are carried out at low monomer conversion, to avoid complexities that might arise due to the gel or Trommsdorff's effect [16]. Also, such studies are carried out using the bulk polymerization method, so as to eliminate all other possibilities of chain transfer from occurring. The contribution of the Co(II) complex to initiation as shown in the cycle has been found to be substantial, even though it is present in catalytic amount [1-2], hence the justification for using the word "catalytic". The abstracted hydrogen has been suggested to come from the α-methyl group, based on the fact that branching was not observed in the polymer chains, which would have given rise to polymer chains with internal unsaturation [3]. The structure of the resulting polymer chain is shown below.

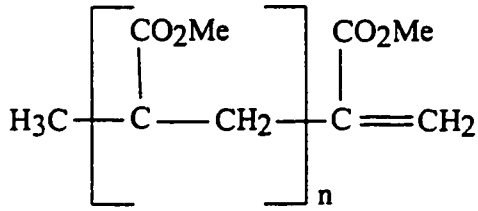


Figure 1.2 Structure of a terminated Poly(methyl methacryate) chain

1.2 Scope and Objectives

It is apparent that solutions have to be found for the problems encountered in using thiols and mercaptans as molecular weight regulators. So far, limited efforts have been channeled towards this end. However, there is a strong need to expand the range of catalytic chain transfer agents presently available, in order to allow for more options and flexibility in choice. It is to this end that we proposed to bis(α-furildioxime)cobalt(II) as a possible catalytic chain transfer agent. We aim to pursue the following specific objectives:

1. Synthesis and characterization of the hydrogen-bonded and BF_2-bridged bis(α-furildioxime)cobalt(II), $[Co(afdo\text{-}2H)_2(BF_2)_2]$ complex.
2. To investigate the catalytic chain transfer potentials of the complex in the polymerization of some acrylates and styrenic monomers.
3. To determine the molecular weight and molecular weight distribution of the resulting polymers using dilute solution viscosity (DSV) and gel permeation chromatography (GPC) techniques.

4. To determine the Catalytic Chain Transfer Constant, Cs of the complex for each system using the Mayo equation.

CHAPTER TWO

LITERATURE REVIEW

2.1 Non-catalytic Chain Transfer Agents

2.1.1Thiols and Mercaptans

Thiols and mercaptans are an important class of compounds widely used in industry to control the molecular weight of polymers. Commercial thiols used for this purpose are usually sold as mixtures containing a wide range of carbon chain lengths. Their effectiveness as chain regulators depends on the type of polymerization system (e.g. bulk, suspension, emulsion etc) and the reaction conditions. Their presence in the reaction mixture introduces certain modifications in the kinetics of the reaction, mechanism of de-sorption and re-absorption, and particle nucleation [20].

A decrease in the rate of polymerization with increasing concentration of the chain transfer agent (CTA) is generally observed in all polymerization systems [18-23]. This decrease in rate in emulsion systems has been attributed to de-sorption of chain transfer radicals from the polymer particle [21, 24]. The decrease is however more prominent with the short chain compounds like

butanethiol or 2-mercaptoethanol, because they are usually more readily soluble and diffusion is less hindered. Another factor worth considering in emulsion systems is the partitioning ratio of the mercaptan between the monomer droplets and the aqueous phase, which is governed by the relative solubility of the transfer agent in the two phases [25]. The chain transfer efficiency of the mercaptans and their effect on the rate of polymerization decreases with increasing chain length. For example, *n*-dodecyl mercaptan was found to have little or no effect on the rate of polymerization of styrene [23, 24], and on its rate of copolymerization with butyl acrylate [20]. When used in the polymerization of di-n-hexyl itaconate [26], and in the suspension polymerization of vinyl chloride [27, 28], products with improved thermal stability were obtained, probably resulting from suppression of the number of terminal double bonds. Hence, it is not in all cases that molecular weight control is desirable. In addition to chain transfer, some mercaptans have been found to act as initiators as well. This is the case with *t*-dodecanethiol in the copolymerization of MMA and styrene [29].

In addition to the control of molecular weight and particle size in emulsion systems, mercaptans have also been used to modify the degree of cross-linkage in the suspension copolymerization of glycidyl methacryalate and ethylene dimethylacrylate. This resulted in desirable modifications of certain parameters such as pore-size distribution, specific surface area and some chromatographic properties that are very important in size exclusion chromatography [30]. The

polymer obtained with butanethiol was found to swell more, owing to decrease in both molecular weight as well as degree of cross-linkage.

Chain transfer activity is not restricted only to thiols. The use of functionalized thiols (mercaptans) in the syntheses of low molecular weight polymers for various applications has also been reported [31]. 2-mercaptoethanol was used to obtain oligomers applicable in reactive injection molding (RIM) and in 'high solids' surface coatings formulations. An average chain transfer constant (C_S) value of 2.44 ± 0.1, was quoted for MMA in suspension polymerizatioin, and was found to be independent of the concentration of the chain transfer agent. Similarly, butanethiol used in the synthesis of poly (vinyl acetate) and poly (vinyl alcohol) having 2-hydroxyethylthio end groups [32], and poly (vinyl chloride) in suspension [27]. Low molecular weight poly (methyl methacrylate-co-n-butyl methacrylate) has also been obtained in emulsion, using iso-octyl-3-mercaptopropionate [33]. These polymers were developed for use as fugitive binders of high temperature powders to be applied in a rapid photocopying method known as selective laser sintering (SLS).

Another class of functionalized thiols used as molecular weight regulators is the thiohydroxamic esters. The polymerization of MMA, methyl acrylate (MA), vinyl acetate (VA) and styrene was studied in the presence of *N*-hydroxypyridine-2-thione and *N*-hydroxy-4-methylthiazole-2(3H)-thione in bulk, at 60°C [34]. In all cases, C_s values in the range 0.32-20 were reported except with vinyl acetate where a value of 80 was reported.

2.1.2 Other Non-Catalytic Chain Transfer Agents

The use of halogenated hydrocarbons to regulate the molecular weight of polymeric products has for long been established. The presence of carbon tetrabromide (CBr_4) [24] and carbon bromotrichloride ($CBrCl_3$) [35] in the emulsion polymerization of styrene has been found to promote the production of low molecular weight free radicals in the latex particle. The active species suspected to be tribromomethyl radical ($CBr_3^{\bullet}$) or its adduct with monomer, was able to escape from the latex particles. Their escape results in a decrease in the total number of free radical in the system compared to the number observed in the absence of the CTA. A consequence of this is a decrease in the rate of polymerization. Carbon tetrabromide has similarly been used in acrylic latex paints formulations. Molecular weight control in poly (methyl methacrylate-co-butyl acrylate) was achieved in this manner [36].

Certain sulfur-containing polymers have been found to exhibit chain transfer ability. Poly (styrene disulfide) and poly (styrene tetrasulfide) were studied as potential chain transfer agents in styrene polymerization [37]. The activity of poly (styrene disulfide) was found to be much higher than that of poly (styrene tetrasulfide). The latter was found to cause some retardation not observed in the former. Molecular weight control has also been achieved in the polymerization of MMA using ketones [38].

$RuCl_2(PPh_3)_3$ and $NiCl_2(PPh_3)_2$, in the presence of alkoxides like $Al(iOC_3H_7)_3$ have been used as chain transfer agents, to control molecular weight of poly(methyl methacrylate) [34, 39]. Ethyl 2-[1-(1-methoxy-1-cyclohexylperoxy)ethyl] propenoate has been used to regulate molecular weight of MMA, and C_s values of 0.102 for MMA, 0.88 for methyl acrylate and 1.02 for styrene all at 60°C have been reported [40].

2.2 Catalytic Chain Transfer Agents

As mentioned earlier, these compounds are so efficient that only parts per million amounts are required to effect considerable reduction in molecular weight. All the catalytic chain transfer agents studied to date have been found to have the following features in common:

1. The central metal atom (usually cobalt(II)) having a single unpaired electron in the d-orbitals.
2. The compounds are cyclic and planar (owing to the square planar geometry of the complexes).
3. They are not strongly coordinated at the axial positions.
4. They are stable (do not decompose) at the temperature of polymerization.
5. They are sufficiently soluble in the monomer

2.2.1 Porphyrin and Phthalocyanins Complexes

Catalysis of chain transfer to monomer was first observed in 1975 in the bulk polymerization of methyl methacrylate (MMA), using cobalt(II) complex of hematoporphyrin tetramethyl ether [2, 17]. The compound by itself does not initiate polymerization, even after prolonged heating. Similarly, small amounts of the complex did not influence the initial rate of polymerization as observed with regular radical initiators like Azo bis(isobutyronitrile), AIBN. However, a sharp decrease in molecular weight was observed upon addition of very small amounts of the compound. Analysis of the number of polymer chains obtained at the end of the reaction showed that 1.2 M chains of macromolecular product were formed in excess of the amount expected based on initiator efficiency and concentration [2].

In addition, kinetics analysis has shown that each molecule of the transfer agent was involved in no less than 2000 acts of chain transfer or cycles [2]. Since no other substances were present besides the monomer, initiator and the transfer agent, it was proposed that cobalt hematoporphyrin tetramethyl ether played a catalytic role in the chain transfer process in the experiment. When the same complex was used in the polymerization of acrylamide in acetic acid, it showed no catalytic activity owing to decomposition [18]. This is indicative of the fact that the integrity of the complex is an important factor in its application as a chain transfer agent.

The catalytic nature of the chain transfer is further supported by the fact that the absorption spectrum of the reacting mixture did not change, when the course of

the reaction was followed spectrophotometrically. Furthermore, practically all of complex added at the beginning of the reaction was recovered at the end [1]. This proved that the complex was not consumed, nor was it bound to the polymer in the course of the experiment. Addition of this compound produced oligomers with terminal double bonds [17]. The resulting unsaturation in the oligomer, coupled with the observations made above, led to the proposal of a generally accepted mechanism of catalytic chain transfer process (Figure 1.1). The structure of a typical cobalt(II) porphyrin complex is shown below.

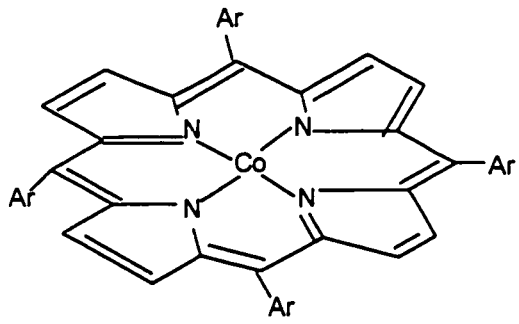


Figure 2.1 tetraarylporphyrincobalt(II)

Polymers of controlled molecular weight have been prepared with a truly homogeneous catalyst system based upon the complexes of tetraphenylporphyrin with aluminum as the central metal atom (TTP)AlX, and propylene oxide as the monomer [41, 42]. The resulting polymers had very narrow molecular weight distribution expected of a living polymerization system. That is, each polymer was capped with an active catalyst species and the number of polymer chains

formed was found to be equal to the number of the catalyst molecules put into the reaction mixture. It was suggested from detailed analyses of initial oligomeric products that the polymerization proceeded through a mechanism in which each chain was capped by the aluminum porphyrin at one end, and the starting chloride at the other. The ring opening polymerization to form oligomers of ethylene and propylene oxides enjoy extensive applications in adhesives, coatings, plasticizers, surfactants, and intermediates in various polyurethanes.

Phthalocyanin complexes are similar to porphyrin in their basic structure, differing only in the nature and position of substituents on the ring. Certain members of this class of compounds have been utilized as chain transfer agents, and have shown catalytic chain efficiency similar to the porphyrins. They are generally applicable in the control of molecular weight in the free radical polymerization of substituted olefinic monomers. They have successfully been applied in the polymerization of methyl methacrylate in the bulk, and in the solution polymerization of acrylamide in acetic acid where an attempt to use porphyrins had failed [18].

The catalytic chain transfer constant value observed was relatively smaller in the later system compared to other monomer systems. The very large propagation rate constant for acrylamide is reported to be responsible for the small chain transfer constant observed. In line with earlier observation [2, 43], a decrease in conversion was observed with increasing concentration of the

complex, probably because it is behaving somewhat as an inhibitor. Figure 2.2 below shows the structure of cobalt (II) 2,16-bis(4-butanamidoyl)phthalocyanin.

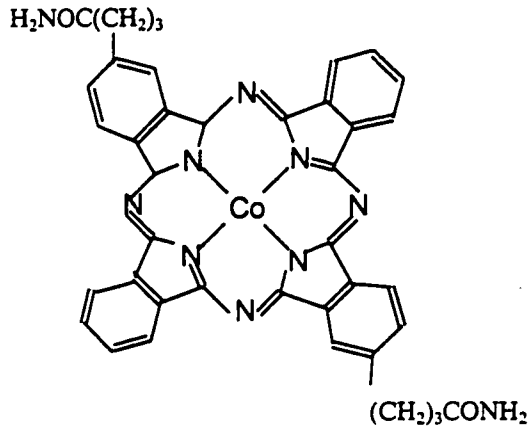


Figure 2.2. 2,16-bis(4-butanamidoyl)phthalocyanincobalt(II)

2.2.2 Cobalt Oximes

Another class of catalytic chain transfer agents based on cobalt(II) is that comprising the cobalt oximes. They are formed by the reaction of a suitable cobalt(II) salt and an appropriate ligand. Examples of ligands utilized are dimethylglyoxime (dmg), diphenylglyoxime (dpg), and others [3, 6, 11, 13, 38 and 43]. The resulting cyclic structures differ in relative stability, depending on the strength of the bridge formed. Stability is an essential prerequisite for any potential CCTA. This class of molecular weight regulators is so far the most efficient, with C_s values of the order of 40,000 [44] reported for BF_2-bridged bis(dimethylglyoxime)cobalt(II). In addition, they are very versatile, easy to

synthesize and cheap compared to the porphyrins. The high cost of porphyrins is creating a barrier in their technological applications [45]. A number of these compounds have been studied and reported in the literature. Most of those reported have already been patented as commercial CCTAs. A brief account of some of them is given below.

2.2.2.1 Hydrogen-bonded bis(dimethylglyoxime)cobalt(II), [Co(dmg-2H)$_2$]

This is the first compound in the group to be studied as a potential catalytic chain transfer agent [46]. Following the first report of O'Driscoll, other workers have undertaken further studies on this compound in an attempt to understand the kinetics and mechanism by which it operates [32, 44]. A wide range of C_S values are reported by several groups for this compound. Values varying dramatically from 20,000 to 2,280, over the molecular weight range of 500 to 186,000 have been reported for bulk polymerization MMA in bulk at 60°C [3]. This wide range was attributed to the dependence of C_S on chain length. This observation contradicts earlier reports which suggested that C_S was independent of chain length [45]. Analysis of the results in one of the patent literature shows a similar pattern pertaining to the decrease in C_S value [46]. They reported C_S in the range 11 to 500 for MMA in the molecular weight range of 8,100 to 88,300. This is remarkably low compared to the values quoted earlier. In all cases reported, C_S

was shown to increase with increase in temperature [44]. The Structure of this compound is shown in Figure 2.3.

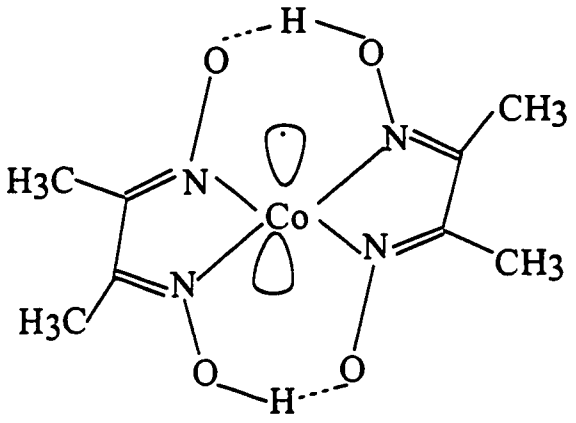


Figure 2.3 Hydrogen bonded bis(alphafurilglyoxime)cobalt(II)

2.2.2.2 BF_2-bridged bis(dimethylglyoxime)cobalt(II)

A number of inherent shortcomings were encountered regarding the use of the hydrogen-bonded compound discussed above. The most important of these shortcomings was its instability towards hydrolysis [44] and oxidation by atmospheric oxygen. This instability is believed to arise from the weak hydrogen bond responsible for maintaining the integrity of the cyclized species. It was thus anticipated that stability would be greatly improved by strengthening this linkage. As expected, stability was enhanced when the hydrogen atom was replaced by a BF_2 moiety. The basic structure of the two compounds remains the same,

differing only in the type of bridging group. The structure of the modified compound is depicted in Figure 2.4.

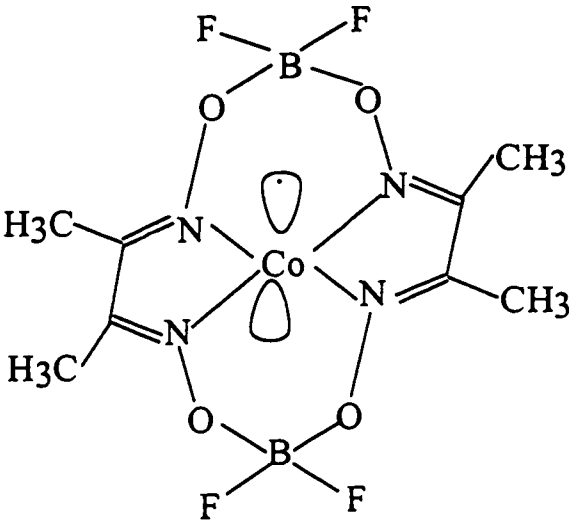


Figure 2.4 BF_2-bridged bis(alphafurilglyoxime)cobalt(II)

A consequence of this increased stability is evident in the C_S values reported for this complex. These values, though generally higher compared to the hydrogen-bonded species, vary over a wide range between 28,000 to 66,000 for MMA in bulk over a temperature range of 60 to 90°C [3]. Other literature reports are even more wide ranging. For example, values ranging from 31,500 to 40,000 for MMA in bulk were quoted for a single temperature of 60°C [44]. To illustrate the extent of variation in C_S, values in the low range of 1,000 to 10,000 have been reported for MMA at the same temperature as above [47]. In all these reports, the dependence of C_S on chain length was noted.

Another important feature of the BF_2-bridged cobalt complex is its tolerance to varying experimental conditions, ranging from drastic to mild. This makes it a really versatile and convenient catalyst for molecular weight control. This tolerance has made it applicable in other polymerization techniques such as suspension, solution and emulsion [3, 9, 17, 43 and 48]. However, not much data has been reported in the literature for emulsion technique. Nevertheless, macromonomers of MMA have been successfully synthesized in emulsion, for use in the preparation of block copolymers [9]. An important factor that affects the efficiency of this catalyst in emulsion systems is its partitioning ratio between the aqueous and the organic phases [43, 49].

Solution polymerization of MMA was conducted in methanol and in butanone of varying degree of purity [49]. The results obtained showed that the polymerization medium (solvent), has strong influence on the chain transfer constant, C_S. Values obtained with undistilled butanone are on the low side, in the range 1700 - 11,000. However, when the butanone was distilled, a dramatic increase was observed, the range increasing to 12,000 - 25,000. The reason for the low values observed in unpurified butanone was attributed to catalyst poisoning by traces of acid present in the solvent. C_S values much lower than these were recorded for polymerization in methanol. The values ranged between 9,500 - 12,000. This may not be unconnected with the fact that the polymer precipitates out in methanol. It is also most likely that there is a strong interaction between the CCTA and methanol, the former being highly soluble in the later.

The polymerization of styrene has been similarly investigated using this CCTA [49]. The lowest C_S values so far, were obtained with styrene, even though much higher concentrations were used. C_S values less than 2000 were reported at 60°C in bulk [44]. This has been explained to be due to the absence of an alpha methyl group in the monomer, which resulted in product with internal unsaturation, in contrast to terminal unsaturation in MMA. The homopolymerization of n-butyl methacrylate and its copolymerization with MMA, conducted in semi-batch emulsion has also been studied [43].

2.2.2.3 BF_2-bridged bis(diphenylglyoxime)cobalt(II)

The dramatic performance of the BF_2-modified bis(dimethylglyoxime)cobalt(II), has led to a series of attempts to expand the collection of cobalt-based CCTAs by studying square planar complexes of cobalt with other glyoxime ligands. The basic requirements of planarity and stability must however be satisfied. Chain transfer activity has been tested on BF_2-bridged bis(diphenylglyoxime)cobalt(II) [9, 43-44]. Results for the polymerization of MMA in bulk using this compound showed a constant C_S over a wide mass range. However, the values obtained are lower in this case [44], compared to those for dimethylglyoxime discussed earlier. This could possibly be due to catalyst purity or larger surface area compared to (dimethylglyoxime)cobalt(II) as shown in Figure 2.5. Alternatively, the interaction of this catalyst with the polymer may be stronger, resulting in a strong Co—alkyl bond. However, this is not likely from a consideration of steric effect

[44]. C_S values reported for styrene fall between 600-700, indicating once again, that for styrene, chain transfer is not diffusion controlled.

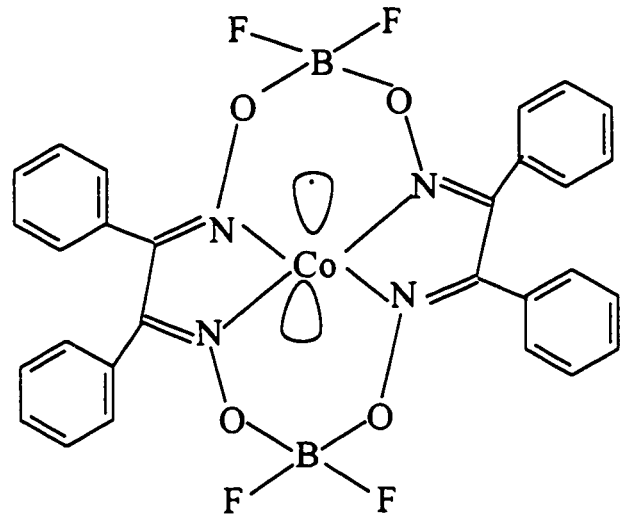


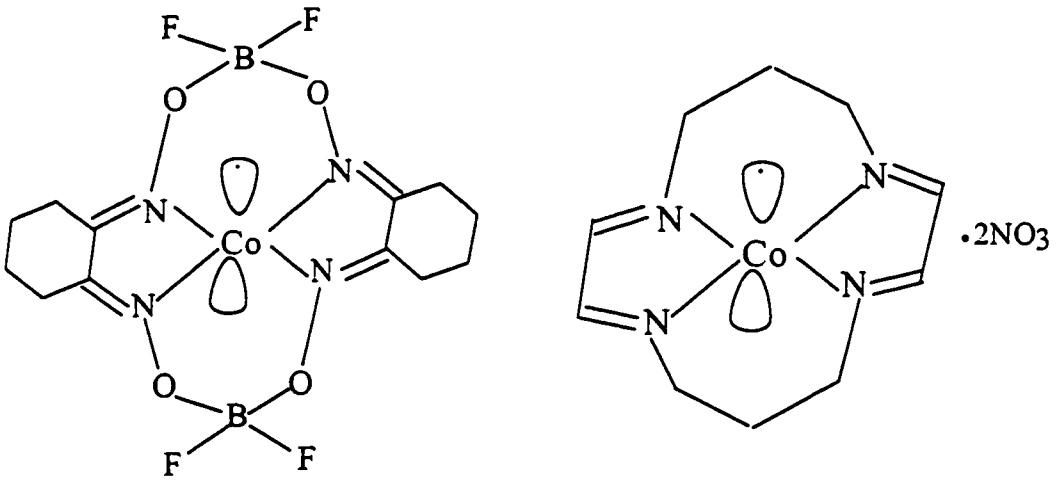
Figure 2.5 BF_2-bridged bis(phenylglyoxime)cobalt(II)

The activity of the same complex modified by coordination with pyridine has been used in emulsion for MMA [9]. The results showed that it is less efficient than its dimethylglyoxime counterpart. This has been suggested to result from the low solubility of the complex in water. However, when polymerization was carried out in butanone solution, the molecular weight of poly(methyl methacrylate) dropped from 1,300,000 to 2590, indicating that efficiency has obviously improved with solubility [9].

Another system studied with this catalyst is the homopolymerization of *n*-butyl methacrylate and its copolymerization with MMA in emulsion. As shown in previous reports, the catalyst was found to partition completely in the organic

phase [43]. A consequence of this insolubility is seen in the comparison of the catalyst with the cobalt dimethylglyoxime. A significant difference in behavior translating into molecular weight and molecular weight distribution was noted, as against the results obtained in solution technique for both catalysts [44].

Other complexes studied as potential catalytic chain transfer agents in this class are shown in Figure 2.6.



a **b**

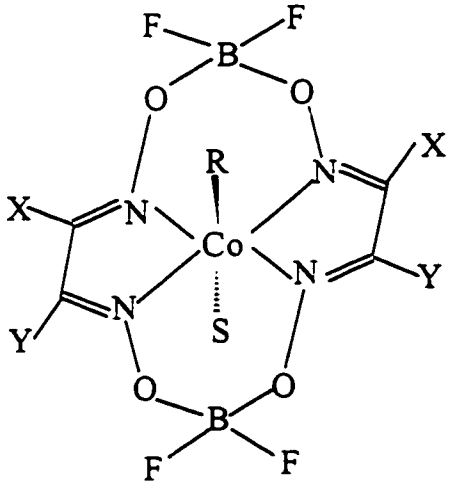
Figure 2.6 Other Catalytic Chain Transfer Agents based on Cobalt(II)

Both of these compounds have shown chain transfer activity, though C_S values obtained were much lower than those for (dimethylglyoxime)cobalt(II) [44]. Values reported for MMA in bulk using '**a**' range between 900-1,300 at 60°C and reaction time of 15 minutes. This has been attributed to the larger cross-sectional area of the catalyst. Similarly, '**b**' was studied in the solution

polymerization of MMA in methanol, run for 30 minutes at 60°C [44]. C_S values less than 100 were recorded. It could not be studied in bulk because it was insoluble in MMA.

2.2.2.4 Catalytic Chain Transfer Agents based on Cobalt(III)

Catalytic chain transfer activity involving cyclic cobalt(III) complexes has been suggested [50]. Alkyl cobalt(III) complexes have been reported to have certain advantages over those of cobalt(II), for example stability to air in the solid state and to hydrolysis in solution [9]. Figure 2.7 shows several of these complexes used in the emulsion polymerization of MMA to obtain macromonomers for the synthesis of graft copolymers.



$iPrCo(III)(DMG\text{-}BF_2)_2$	R = isopropyl., X = Y = methyl, S = H_2O
$MeCo(III)(DMG\text{-}BF_2)_2$	R = methyl, X = Y = methyl, S = H_2O
$MeCo(III)(DEG\text{-}BF_2)_2$	R = methyl, X = Y = Ethyl, S = H_2O
$MeCo(III)(EMG\text{-}BF_2)_2$	R = methyl, X = methyl , Y = ethyl, S = H_2O
$MeCo(III)(CHG\text{-}BF_2)_2$	R = methyl, X = Y = - (C_4H_8)- S = H_2O
$EtCo(III)(DPG\text{-}BF_2)_2$	R = ethyl, X = Y = phenyl, S = H_2O

Figure 2.7 Some Catalytic Chain Transfer Agents based Cobalt (III)

An activity series has been drawn up for some of these catalysts in the emulsion polymerization of MMA [9]. Efficiency was found to increase in the order: EtCo(III)(dpg-BF_2)$_2$ < iPrCo(III)(chg-BF_2)$_2$ < iPrCo(III)(dmg-BF_2)$_2$ < MeCo(III)(emg-BF_2)$_2$ < MeCo(III)(deg-BF_2)$_2$. However, a different order of activity was observed in solution, indicating that the chemistry involved is different. This suggests that activity may not be simply a function of the inherent reactivity of the complex. The influence of the extent of partitioning of the complex in the two phases is evident. Surprisingly, the cobalt(III) complexes have been found to be 3-4 times more efficient than their cobalt(II) counterparts [9].

CHAPTER THREE

EXPERIMENTAL PROCEDURE

3.1 Materials and Apparatus

Methanol, chloroform, butanone, ethanol, cobalt acetate, α-furildioxime, and boron trifluoride (Fluka) were used as received. Tetrahydrofuran and trichlorobenzene (Fisher) were HPLC grade. Monomers (Fluka) were freed from inhibitor by distillation. Liquid nitrogen was used to freeze reaction mixture during degassing. Nitrogen gas (99.5% purity) was used to flush reaction mixture in section 3.3.2. Apparatus used include Ubbelohde viscometers, (from Cannon and Wescan Instruments Inc.), Stopwatch (Venlab Instruments), Eager 200 elemental analyzer. Two Waters gel permeation chromatograms models (equipped with Millennium 2010 and Maxima 800 softwares), Perkin Elmer UV/visible spectrophotometer, Joel Lambda 500 MHz Nuclear Magnetic Resonance Spectrometer, Mettler AE 200 electric balance, pyrex tubes, and vacuum line.

3.2 Preparation of BF_2-bridged bis(α-furildioxime)cobalt(II) Complex

Synthesis of the chain transfer agent was carried out using two experimental procedures reported in the literature [48-51]. These procedures were applied in the syntheses and characterization of BF_2-bridged cobalt(II) oxime complexes in general [48-51], and in the syntheses of cobalt(II) dimethylglyoxime and other related complexes used as catalytic chain transfer agents in particular [3, 38, 42]. These synthetic routes are outlined below.

3.2.1 Synthesis via the Hydrogen-bonded Precursor

Exactly 95.6 mg (0.43 mmol) of α-furilglyoxime (afdo) were weighed on a Mettler AE 200 electric balance and dissolved in 10 ml analytical grade methanol. To this solution was added 49.6 mg (0.20 mmol) cobalt acetate tetrahydrate $Co(O_2CCH_3)_2 \bullet 4H_2O$. The mixture was stirred for about 30 minutes, after which an orange brown precipitate of $[Co(afdo\text{-}2H)_2]$ formed. The precipitate was filtered off using a Buckner funnel, rinsed with cold distilled water, and dried under vacuum at room temperature for 20 hours to obtain 55.6 mg of the product, the yield being 47.0 %. The reaction is represented by the equation below.

$$Co(CH_3CO_2)_2.4H_2O + 2afdo \xrightarrow[30\ min]{Stir} [Co(afdo\text{-}2H)_2].2H_2O + 2CH_3CO_2H \quad (1 + 2H_2O$$

3.2.1.1 Cyclization Reaction

From the product obtained in section 3.2.1, 55.0 mg (0.10 mmol) were weighed and added to 10 ml anhydrous ether in a 50 ml capacity round bottomed flask. To this mixture, about 1.0 ml (0.44 mmol) freshly distilled boron trifluoride etherate solution (BF_3-Et_2O) was added. The mixture was stirred at room temperature for 24 hours. The reddish brown product formed was precipitated by addition of distilled water to the reaction mixture, and filtered. It was rinsed repeatedly with distilled water and dried under vacuum at room temperature to obtain 21.6 mg of the product, the yield being 33.1 %. The synthesis is illustrated by the reaction given below. The final product obtained by this method was labeled 'A'

$$[Co(afdo\text{-}2H)_2].2H_2O + BF3.Et_2O \xrightarrow[24\ hrs]{Stir} [Co(afdo\text{-}2H)_2(BF_2)_2].2H_2O \quad (2)$$

3.2.2 Direct Synthesis

The BF_2-bridged complex was also synthesized directly by dissolving 49.0 mg (0.20 mmol) of cobalt acetate tetrahydrate $Co(O_2CCH_3)_2 \bullet 4H_2O$ in an anhydrous ether solution containing 97.2 mg (0.44 mmol) of α-furilglyoxime. To this mixture, 2.0 ml (0.88 mmol) of freshly distilled BF_3-Et_2O solution was added. The reaction mixture was stirred at room temperature for 24 hours. . The reddish brown product formed was precipitated by addition of distilled water to the

reaction mixture, and filtered. It was rinsed repeatedly with distilled water and dried under vacuum at room temperature. The amount of product recovered was 66.5 mg and the yield was 57.0 %. The reaction is represented by the following equation.

$$Co(CH_3CO_2)_2.4H2O + 2afdo + BF3.Et_2O \xrightarrow[\text{Stir,24 hrs}]{\text{anhydrous ether}} [Co(afdo\text{-}2H)_2(BF_2)_2].2H_2O + 2CH_3CO_2H + 2H_2O \quad (3)$$

The complex obtained in this experiment was labeled 'B'. The two complexes were characterized and subsequently studied for chain transfer activity in the free radical polymerization of methyl methacrylate (MMA) using azo-bis(isobutyronitrile) (AIBN) as initiator.

3.2.3 Characterization of Complexes

Standard spectroscopic methods of chemical analysis such as Ultraviolet/Visible absorption spectroscopy, Infrared absorption spectroscopy, elemental analysis, melting point (decomposition temperature) and solubility (in monomers), were used to characterize the products obtained in sections 3.2.1, 3.2.1.1 and 3.2.2 respectively. The complexes were analyzed for carbon, nitrogen and hydrogen respectively, on an Eager 200 elemental analyzer. The result obtained was compared with calculated values based on molecular weight of 628.89 g/mole for the compound [49].

3.3 Polymerization Reactions

Bulk polymerization technique was employed in this study. The choice of this technique was necessitated by the nature of the study. In general, for a successful study of catalytic chain transfer, the experiment should be designed in such a way that the chances of other chain transfer reactions occurring are either eliminated or minimized. Such chain transfer reactions may arise as a result of interactions between the propagating chain and a monomer molecule, which is called chain transfer to monomer. The propagating chain may also be transferred to a solvent molecule, initiator fragment, or to some impurity present in the reaction mixture. In bulk polymerization technique, only monomer, initiator and propagating chains are present at any stage in the reaction. Consequently, the choice of initiator is as important as the choice of the polymerization technique. The initiator chosen should offer minimum/no interference in the course of the experiment. That is, it should have very low chain transfer constant.

Azobis(isobutyronitrile) (AIBN) was chosen as the initiator because it satisfies the condition stated above, with respect to the monomers to be studied (see Table A4 in Appendix A). Other reasons for its choice include availability, solubility in a wide range of monomers and ease of handling. In designing the experiment, the effect of heat transfer on the kinetics of the reaction was not taken into consideration because monomer conversion was restricted to low level. At such levels, the viscosity of the reaction mixture is not high enough to cause any serious threat of explosion (due to heat transfer problem), or to impinge on the

mobility of the molecules of the chain transfer agent. Similarly, the effect of increased rate of reaction(s), caused by local overheating is usually not significant at such conversion levels. The minimum temperature for polymerization was 60°C (± 1°C). This was sufficient to decompose the initiator molecules into radicals, and at the same time, low enough to prevent high initiation rate, which may give rise to high conversion that will ultimately impinge on the mobility of the chain transfer agent molecules.

3.3.1 Purification of Monomers

All monomers used in the polymerization reactions were freed from the inhibitor prior to use. The procedure outlined below was followed. The monomer was mixed with portions of 10 % aqueous sodium hydroxide solution and shaken, until all inhibitor present in the monomer has transferred from the organic into the aqueous phase. In case of styrene, this was continued until the aqueous phase did not show any brick red coloration. After allowing ample time for the two phases to separate, the aqueous phase was drained off and discarded in each case. This step was followed by repeated rinsing of the organic phase with distilled water, until all traces of sodium hydroxide have been removed. Finally, a substantial amount of anhydrous sodium sulfate or calcium chloride was added to the monomer, shaken vigorously and allowed to stand for about two hours. This was done to remove all traces of water from the monomer. The anhydrous monomer was stored in the refrigerator prior to distillation. The monomer was distilled at

room temperature, under reduced pressure, to prevent premature polymerization at elevated temperature.

3.3.2 Design of Polymerization Experiments

The polymerization procedure was optimized after carrying out preliminary reactions to ascertain the effect of dissolved oxygen on the polymerization reaction. In the preliminary runs, 2,2′-azobis(isobutyronitrile), AIBN was used in the absence of the chain transfer agent. A known amount of the initiator was dissolved in a measured volume of freshly distilled MMA, to obtain a solution of known concentration. Two 50 ml capacity round-bottomed flasks fitted with glass stoppers were each charged with 10 ml from the above solution. The flasks were immersed in an oil or water bath maintained at 60°C (± 1°C). Reaction was allowed to proceed for one hour. Afterwards, the contents of the flasks were emptied into a large excess of methanol, to precipitate the polymer that may have formed. No polymer was obtained indicating that reaction did not take place.

The experiment was repeated using the setup in Figure 3.1. A three-neck flask was connected to a condenser fitted with a drying tube filled with anhydrous calcium chloride. High purity nitrogen gas was passed through a second opening using a needle and a rubber septum. The third opening was sealed with a rubber septum and a tiny hole made to serve as outlet for any displaced air (oxygen) or excess nitrogen. A gentle stream of the nitrogen gas was passed through the flask maintained at 60°C (± 1°C) for one hour, after which the contents were

precipitated in methanol. The methanol turned turbid, yielding a white gelatenous precipitate of poly (methyl methacrylate).

The product was subsequently filtered, rinsed with methanol and dried under vacuum at room temperature. The weight of the dried polymer sample was taken and the per cent conversion calculated from the initial mass of monomer used. The experiment was repeated under the same conditions and the mass of the polymer and per cent conversion similarly determined. The conversions from the two runs were substantially different. See the setup in Figure 3.1, page 37.

Finally, a vacuum line was used to ensure complete removal of air from the monomer solution. Two types of polymerization tubes were designed using 50 mL capacity pyrex test tubes. The first design was simply a modification of the Schlenck tube, with a sidearm grafted near the top of the tube that served both as inlet for the monomer solution and outlet for the polymerization product, respectively. A schematic diagram of this Schlenck reactor tube is shown in figure 3.2a. The tubes were promptly placed in a water bath maintained at 62°C (± 1°C) for one hour, after degassing according to the procedure described in section 3.3.3. The polymer formed was treated according to the procedure outlined in section 3.3.4. Again, significant variations in the per cent conversion were observed. Obviously, a leak must have occurred in the vacuum that allowed atmospheric oxygen to interfere with the reaction. Hence, the idea of using the modified Schlenk tube for polymerization was abandoned.

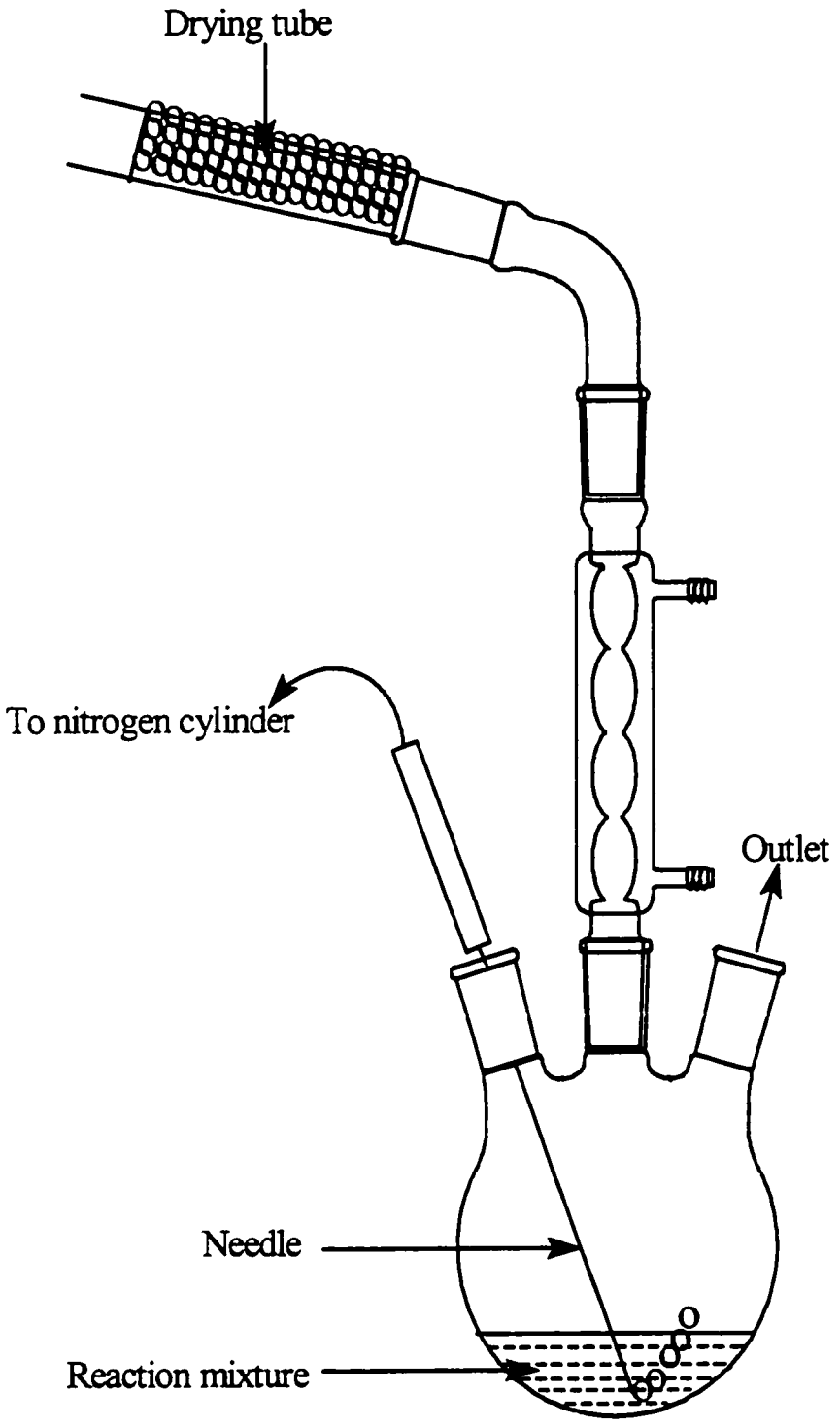


Figure 3.1 Simple Polymerization Reaction Setup

Finally, the design commonly used and reported in the literature [45] was adopted. A 50 ml capacity pyrex test tube was connected to a ground female joint through a narrow neck, which was made long enough to facilitate ease of sealing after the freeze-thaw cycles. In this design, the degassed, frozen monomer was sealed under vacuum using flame. In this way, the contents of the tube were permanently isolated from the atmosphere for the duration of the reaction. Polymerization reactions were run in five reaction tubes under the same experimental conditions, to test the effectiveness of this design. The per cent conversions calculated were within acceptable range, discounting experimental error. This design was therefore adopted for use in all the polymerization reactions. A schematic diagram of the tube is shown in figure 3.2b.

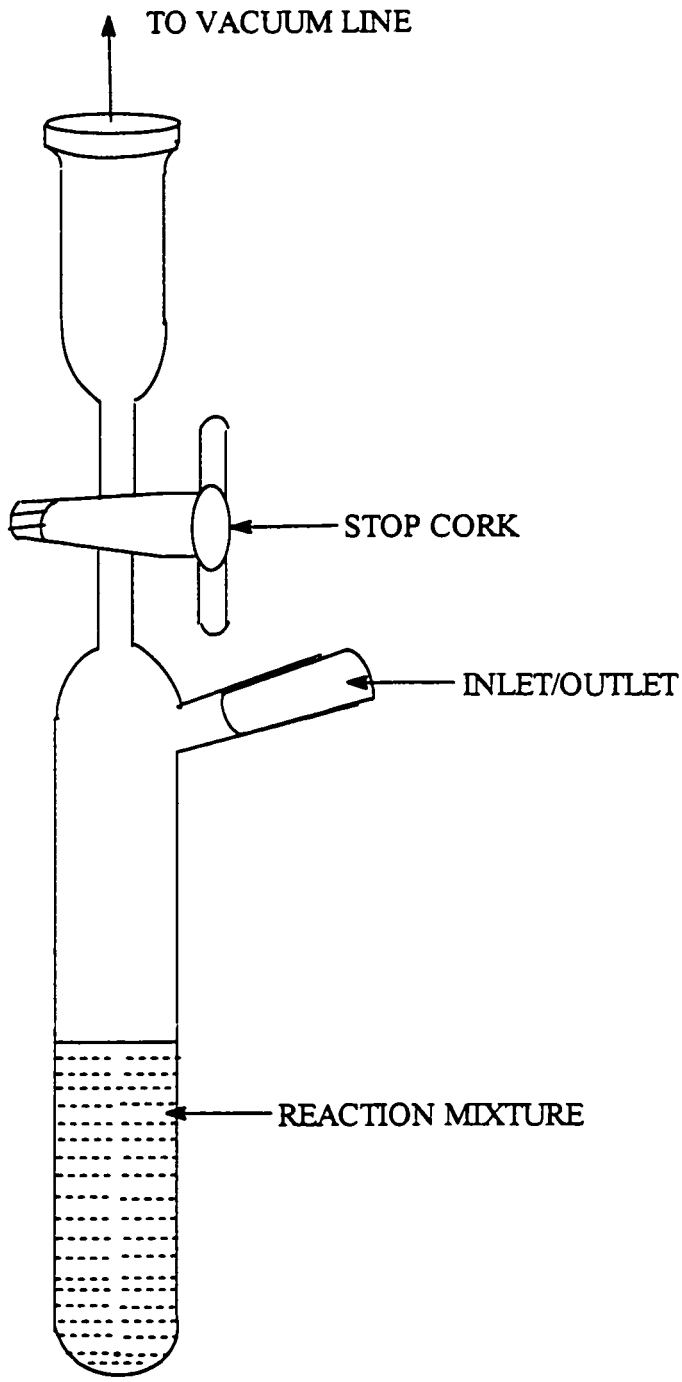


Figure 3.2a Modified Schlenk Reaction Tube

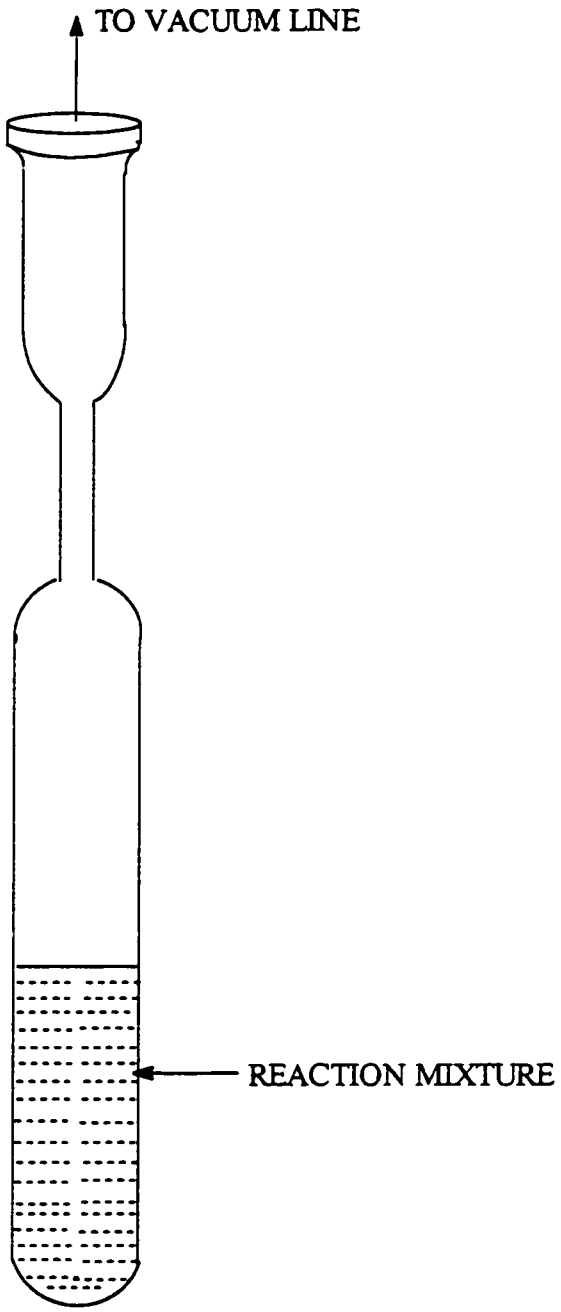


Figure 3.2b Simple Disposable Reaction Tube

3.3.3 General Procedure for Degassing Monomer Solution

The tubes once charged with the monomer solution were degassed using a high efficiency vacuum pump. Each tube was degassed successively by several freeze-thaw cycles. Degassing process was done as follows. Each tube was hooked to the vacuum line and immersed in a Dewar flask containing liquid nitrogen, with the vacuum shut off. The tubes were kept in the liquid nitrogen, until the contents were completely frozen. Next, vacuum was applied and sustained long enough to evacuate the air above the frozen solution. The vacuum was then shut off and the contents thawed by immersing the tubes in a beaker of water. Air bubbles trapped in the frozen solution were observed to escape to the evacuated surface as the frozen solution melted. Several freeze-thaw cycles were repeated until as much air as possible was removed from the solution. All the tubes in a particular run were subjected to the same number of freeze-thaw cycles. However, the relative number of these cycles differed from one monomer to another.

3.3.4 General Procedure for Treatment of Polymer Samples

At the end of the polymerization reaction, the contents of each tube were removed from the water bath and promptly placed in a beaker of ice cold water, to stop further reaction. The seals on the tubes were broken and the contents poured into beakers containing methanol. The contents of each beaker were stirred vigorously to precipitate the polymer formed. The precipitated product was rinsed several

times with methanol and filtered using Whatman filter paper. The clean polymer was then placed in the oven and dried to constant weight at room temperature under vacuum. The mass of product from each tube was determined and the per cent conversion calculated.

3.3.5 Screening of Catalytic Chain Transfer Agent

The standard experimental procedure for catalytic chain transfer study cited in the literature [9, 45] and followed throughout this work was first verified in the polymerization of MMA using DuPont's bis(dimethylglyoxime)cobalt(II) as CCTA. This was done in order to establish the reproducibility of the general trend observed and reported in the literature for this and similar systems. The results obtained in this preliminary investigation are given in Appendix A4.

The complexes prepared in sections 3.2.1.1 and 3.2.2 were tested for chain transfer activity in the polymerization of MMA. The experiment was conducted as follows. A stock solution 2.0 mM in AIBN was prepared. Stock solutions containing 0.134 mmol of the complexes (designated A and B) in 10.0 ml methyl methacrylate (MMA) were also prepared. Two reaction tubes were charged with 10.0 ml of the MMA/AIBN solution. Appropriate volumes of the MMA/CCTA solutions were added to make the concentration of the CCTA 4.85 micromolar in each. A third tube containing 8.0 ml MMA/AIBN solution and no CCTA was used as control.

The tubes were degassed and sealed following the procedure described in section 3.3.3. They were immediately transferred to a water bath regulated at 62°C (± 1°C) and reaction was allowed to proceed for 45 minutes. The contents of each flask were treated according to the procedure outlined in section 3.3.4 above. The effect of the complexes on the molecular weight of the products was studied using dilute solution viscometry and the Mark-Houwink equation.

3.3.6 Polymerization of Methyl methacrylate (MMA)

Two stock solutions one 0.134 mM CCTA in MMA and the other 2.0 mM AIBN in MMA were prepared using freshly distilled monomer. Aliquots of 10.0 ml were added to five clean, dry reaction tubes. To these five tubes were added 0.00, 0.04, 0.08, 0.15 and 0.36 ml of the MMA/CCTA solution respectively. The tube containing no complex served as control. The tubes were degassed and sealed using the procedure outlined in section 3.3.3 above, and promptly transferred into a water bath regulated at 61°C (± 1°C). After reaction has proceeded for 90 minutes, the tubes were treated according to the procedure in section 3.3.4, and the molecular weights of the polymer samples determined using dilute solution viscometry (DSV) and gel permeation chromatography (GPC).

3.3.7 Polymerization of Butyl methacrylate (BMA)

A 0.127 mM stock solution of the CCTA was prepared by dissolving 0.8 mg of the complex in 10.0 ml of freshly distilled BMA. A second stock solution, 2.0 mM AIBN in BMA was prepared by dissolving 21.7 mg of AIBN in 65.0 ml BMA. Five clean, dry reaction tubes were charged with 10.0 ml aliquots of the AIBN/BMA solution. To these tubes were added 0.00, 0.06, 0.12, 0.18 and 0.24 ml of the stock CCTA/BMA solution respectively. The tube containing no CCTA served as control. The contents of the tubes were degassed and sealed following the procedure described in section 3.3.3, and immediately placed in a water bath maintained at 60°C (± 1°C). The tubes were promptly removed from the bath after 90 minutes, and placed in cold water to stop further reaction. The contents of each were treated following the procedure outlined in section 3.3.4. Molecular weight analysis was subsequently carried out on the samples.

3.3.8 Polymerization of 2-Ethylhexyl methacrylate (2-EHMA)

Six clean dry reaction tubes were each charged with 10.0 ml of a 2.0 mM solution of AIBN, prepared by dissolving 21.7 mg of the initiator in 10.0 ml 2-EHMA. To these tubes were added 0.00, 0.06, 0.12, 0.18, 0.24 and 0.30 ml of 0.127 mM CCTA/EHMA solution, similarly prepared by dissolving 0.8 mg of the CCTA in the monomer. The sixth tube served as control, with no CCTA. The tubes were degassed and sealed according to the procedure in section 3.3.3, and promptly

transferred to a water bath regulated at 66°C (± 1°C). After 90 minutes, the resulting polymer was treated as outlined in section 3.3.4. The molecular weights of the samples were subsequently analyzed.

3.3.9 Polymerization of Butyl Acrylate (BA)

A 0.127 mM stock solution of the CCTA was prepared by dissolving 0.8 mg of the complex in 10.0 ml of freshly distilled BA. A second stock solution, 2.0 mM in BA was prepared by dissolving 21.7 mg of AIBN in 65.0 ml BA. Six clean, dry reaction tubes were charged with 10.0 ml aliquots of the AIBN/BA solution. To these tubes were added 0.00, 0.06, 0.12, 0.18, 0.24 and 0.30 ml of the stock CCTA/BA solution, respectively. The tube containing no CCTA served as control. The contents of the tubes were degassed and sealed following the procedure described in section 3.3.3, and immediately placed in a water bath maintained at 60°C (± 1°C). The tubes were promptly removed from the bath after 90 minutes, and placed in cold water to stop further reaction. The contents of each were treated following the procedure outlined in section 3.3.4. Molecular weight analysis was subsequently carried out on the samples.

3.3.10 Polymerization of 2-Hydroxyethyl methacrylate (2-HEMA)

Six clean dry reaction tubes were each charged with 10.0 ml of a 2.0 mM solution of AIBN, prepared by dissolving 0.8 mg of the initiator in 10.0 ml 2-HEMA. To

these tubes were added 0.00, 0.06, 0.12, 0.18, 0.24 and 0.30 ml of 0.127 mM CCTA/2-HEMA solution, similarly prepared by dissolving 0.8 mg of the CCTA in the monomer. The sixth tube served as control, with no CCTA. The tubes were degassed and sealed following the procedure in section 3.3.3, and promptly transferred to a water bath regulated at 60°C (± 1°C). After 90 minutes, the contents of each tube were treated as outlined in section 3.3.4, and the molecular weights of the polymer samples analyzed.

3.3.11 Polymerization of 2-Hydroxypropyl methacrylate (2-HPME)

Ten mililiter aliquots of a 2.0 mM solution of AIBN were put into six clean dry reaction tubes. The solution was prepared by dissolving 0.8 mg of the initiator in 10.0 ml 2-HPMA. To these tubes were added 0.00, 0.06, 0.12, 0.18, 0.24 and 0.30 ml of 0.127 mM CCTA/2-HPMA solution prepared by dissolving 0.8 mg of the CCTA in the monomer. The sixth tube served as control, with no CCTA. The tubes were degassed and sealed following the procedure in section 3.3.3, and promptly transferred to a water bath regulated at 60°C (± 1°C). After 90 minutes, the contents of each tube were treated as outlined in section 3.3.4. Molecular weight was analyzed by DSV and GPC techniques respectively.

3.3.12 Polymerization of Styrene (Trial one)

A 0.127 mM solution of the CCTA in styrene was prepared by dissolving 0.8 mg of the complex in 10.0 ml freshly distilled monomer. A stock solution containing 2.0 mM AIBN in styrene was similarly prepared by dissolving 21.3 mg in 65.0 ml monomer. Five clean, dry reaction tubes were each charged with 10.0 ml of the AIBN/Styrene solution. To these tubes were added 0.00, 0.06, 0.12 0.18 and 0.24 ml of the CCTA/Styrene solution respectively. The tube containing no CCTA served as control. The tubes were degassed and sealed according to the procedure outlined in section 3.3.3, and promptly transferred into a water bath maintained at 73°C (± 1°C). Reaction was allowed to proceed for two hours, at the end of which the contents of each tube were treated according to the procedure described in section 3.3.4. The molecular weight of the polymer samples obtained were similarly analyzed using DSV and GPC techniques.

3.3.13 Polymerization of Styrene (Trial two)

A second experiment was conducted using higher concentrations of the CCTA. Six clean, dry reaction tubes were each charged with 10.0 ml of 2.0 mM solution of styrene/ AIBN, prepared by dissolving 21.7 mg of the initiator in 65.0 ml of the monomer. To these tubes were added 0.00, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of freshly prepared stock CCTA/styrene solution of the same concentration as that used in section 3.3.13. The tube containing no CCTA served as control. The tubes were

degassed and sealed following the procedure outlined in section 3.3.3. They were instantly transferred into a water bath regulated at 76°C (± 1°C). After three hours (3 hrs.), the tubes were treated according to the procedure of section 3.3.4.

3.3.14 Polymerization of Styrene Oxide

A 2.0 mM solution of AIBN in styrene oxide was prepared by dissolving 21.7 mg of the initiator in 65.0 ml of monomer. Six reaction tubes were each charged with 10.0 ml of this solution. This was followed by the addition of 0.00, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of a 0.127 mM solution of the CCTA in styrene oxide, prepared by dissolving 0.8 mg of the initiator in 10.0 ml monomer. The tube containing no CCTA served as the control. The tubes were degassed and sealed as described in section 3.3.3, and then transferred to a water bath maintained at 72°C (± 1°C). After two hours, the contents of each tube were treated according to the procedure in section 3.3.4. No polymer was obtained, indicating that polymerization did not occur.

3.3.15 Copolymerization of Styrene and Methyl methacrylate

21.7 mg of AIBN was added to a mixture containing 33.0 ml each, of styrene and MMA, to obtain a stock solution containing 2.0 mM AIBN in the monomer mixture. Another stock solution containing 0.224 mM CCTA in styrene was prepared by dissolving 0.7 mg of the CCTA in 5.0 ml styrene. Aliquots of 10.0 ml

from the AIBN stock solution was placed in six reaction tubes followed by the addition of 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 ml of CCTA/styrene solution, respectively. The tube containing no CCTA served as the control. The tubes were degassed and sealed following the procedure described in section 3.3.3 and immediately transferred to a water bath maintained at a temperature of 60°C (± 1°C). They were removed from the bath after 90 minutes and placed in ice-cold water to quench the reaction. The contents were treated as described in section 3.3.4. Molecular weight analysis was carried out using DSV and GPC techniques.

3.3.16 Copolymerization of Styrene and Butyl methacrylate

A 2.0 mM solution was prepared by dissolving 21.8 mg of AIBN in a mixture containing 33.0 ml of freshly distilled styrene and BMA respectively. A 0.224 mM stock solution of the CCTA was similarly prepared by dissolving 0.7 mg in 5.0 ml styrene. Six clean, dry reaction tubes were each charged with 10.0 ml of the styrene/BMA mixture, followed by addition of 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50 ml of the CCTA solution to the tubes respectively. The tube containing no CCTA served as control. The tubes were degassed and sealed according to the procedure outlined in section 3.3.3, and immediately transferred to a water bath regulated at 61°C (± 1°C). They were removed after 90 minutes and treated according to the procedure outlined in section 3.3.4.

3.3.17 Copolymerization of Methyl methacrylate and Butyl methacrylate

A 2.0 mM solution was prepared by dissolving 21.8 mg of AIBN in a mixture containing 33.0 ml each, of freshly distilled MMA and BMA respectively. Another solution 0.224 mM in strength was prepared by dissolving 0.7 mg of the CCTA in 5.0 ml MMA. Ten mililiter of the mixture was put in each of six reaction tubes. This was followed by addition of 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50 ml of the CCTA solution respectively. The tube containing no CCTA served as control. The tubes were degassed and sealed following the outlined procedure in section 3.3.3, and immediately transferred into a water bath maintained at 60°C (± 1°C). After 90 minutes, the tubes were removed and the contents treated as described in section 3.3.4.

3.4 Polymer Characterization

The polymer samples obtained in the experiments described in sections 3.3.6 - 3.3.17 were characterized by FT-IR and ^{1}H-NMR spectroscopic techniques, respectively. Molecular weight was determined using dilute solution viscometry and gel permeation chromatography techniques. The various characterization techniques employed are described below.

3.4.1 FT-Infrared Spectroscopy of Polymer Samples

FT-Infrared spectra of the samples were taken either in the solid state, or as thin films of the polymer prepared in spectrum grade chloroform. The spectra of polystyrene and poly(methyl methacrylate) samples were taken in the solid state in the form of potassium bromide pellets. Those of other samples were taken in the form of thin film of the polymer in chloroform, because they could not give a homogeneous mixture with potassium bromide due to their gummy, non-crystalline nature. A Perkin Elmer FT-Infrared Spectrophotometer was used. All spectra were taken in the region between 400 to 4000 cm^{-1}.

3.4.2 Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy of Polymer Samples

^{1}H-NMR spectra of the polymer samples were taken on a Joel Lambda 500 MHz nuclear magnetic resonance spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent, with tetramethyl silane, (TMS) as internal standard. The purpose of taking these spectra is to establish the tacticity of the homopolymers synthesized. From the spectra, it is possible to tell the arrangement of pendant groups such as alkyl, phenyl and alkoxyalkyl, on one monomer relative to another. However, for more rigorous study on polymer samples, solid state ^{3}C-NMR is now employed [54]. The preparation of a typical sample for ^{1}H-NMR analysis is described below. An appropriate quantity of the sample was weighed

and dissolved in a vial in deuterated chloroform ($CDCl_3$) to which was added tetramethyl silane (TMS) as internal standard. The resulting polymer solution was filtered using cotton wool with the help a dropper.

3.4.3 Dilute Solution Viscometry (DSV)

Viscosity measurements were conducted at room temperature using two designs of the Ubbelohde viscometer. One of such designs from Wescan Instrument Inc., equipped with an automatic timing device and a thermostat water bath. The other, Cannon 75 E826, was used with a manual stopwatch, at room temperature without water bath. All solvents used were reagent grade. Mark-Houwink constants were taken from the 1976 and 1989 editions of Polymer Handbook (52, 53). The same general procedure outlined below was followed in the viscometry experiment on all samples.

Stock solutions ranging from 0.5 to 1.0 g polymer per 100 ml chloroform or butanone were prepared in all cases. The viscometer was charged with pure solvent and the time taken for the solvent to flow through the bulb noted. Next, 10 ml of the stock solution was transferred into the empty viscometer and the time taken for the solution to pass the same marks noted. The solution was diluted by addition of 3.0 ml aliquots of the solvent, and the time taken to pass the marks noted each time, until readings corresponding to five or six different concentrations were obtained. For each concentration, three readings were taken

and the average used to calculate the relative viscosity. The solution was discarded and the procedure repeated for all samples in the same batch.

3.4.4 Gel Permeation Chromatography (GPC)

Two different models of gel permeation chromatographs were used for the analysis of the polymer samples. These are briefly described below.

(a) Waters high performance liquid chromatograph, HPLC equipped with Millennium 2010 software. Four serially arranged columns packed with 100, 500, 1000 and 10,000 Å ultrastyragel as stationary packing material were used. The four columns have dimensions of 300 mm by 7.8 mm respectively. HPLC grade tetrahydrofuran (THF) was used as eluting solvent. Sample concentration ranged between 1 – 2 % weight per volume solution of the polymer in the mobile phase.

(b) Waters ALC/GPC equipped with Maxima 820 software. The packing material was styragel HT3, HT4 and HT5 respectively (HT = high temperature). The three columns were arranged serially, and have the same dimensions of 300 by 7.8 mm. Trichlorobenzene (TCB), was used as the eluting solvent. Polymer solutions were prepared in the mobile phase. Polystyrene standards were used to calibrate the instruments in both cases.

3.5 Molecular Weight and Molecular Weight Distribution (MWD)

Polymer samples are usually characterized by several molecular weight averages. Two different methods were employed in characterizing the molecular weights of the polymer samples in this study. These methods produce molecular weight averages that are numerically different, because the techniques measure different properties of the polymer. The techniques are outlined below.

3.5.1 Viscosity Average Molecular Weight (M_V)

The molecular weight determined from dilute solution viscometry is called viscosity average molecular weight, M_V, which is obtained through the Mark-Houwink equation given below.

$$\log[\eta] = \log K + a \log \overline{M}_v \qquad (1)$$

K and *a* are constants for a particular polymer/solvent pair at a specified temperature.

$[\eta]$ = Intrinsic viscosity (viscosity at infinite dilution)

M_V = viscosity average molecular weight

Viscometry is an approximate and indirect method of determining molecular weight, because there is to date, no established theory relating the viscosity of a

polymer solution to chain length. The Mark-Houwink equation cannot directly relate absolute polymer viscosity to molecular weight, because the two constants in the equation must first be determined by absolute methods, such as light scattering, osmotic pressure, sedimentation, etc. The intrinsic viscosity is the intercept of the plot of the reduced or inherent viscosity versus concentration of the polymer sample. The various relationships utilized are given below.

$$\eta_{rel} = \frac{t_o}{t_{solvent}} \qquad (2)$$

$$\eta_{sp} = \eta_{rel} - 1 \qquad (3)$$

$$Reduced\ Viscosity = \frac{\eta_{sp}}{C} \qquad (4)$$

$$Inherent\ Viscosity = \ln\frac{\eta_{rel}}{C} \qquad (5)$$

C = concentration of polymer solution

3.5.2 Determination of Chain Transfer Constant (C_S) from Dilute Solution Viscometry (DSV)

Catalytic chain transfer constant is a number that gives a measure of the efficiency of a transfer agent. The higher this number is, the more efficient is the transfer agent. The molecular weights obtained from the Mark-Houwink equation was used with the Mayo equation to calculate the chain transfer constant, C_S of the CCTA for each system. The C_S value can be obtained in two ways: from the Mayo equation applied to a single point (molecular weight) (13). This will yield a C_S value for each sample in a given batch. The second approach is to obtain a single C_S value from a plot of the reciprocal of the degree of polymerization versus the ratio of the concentration of the CCTA to that of the monomer (3, 6, 13). The second approach was used in this study. The simplified Mayo equation is given below.

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP_o}} + C_C \frac{[CCTA]}{[Monomer]} \qquad (6)$$

Where

$$\frac{1}{\overline{DP_o}} = C_M + C_I \frac{[I]}{[Monomer]} + C_S \frac{[Solvent]}{[Monomer]} + ... \quad (7)$$

C_C, C_M, C_I, C_S are chain transfer constants for transfer to monomer, initiator and solvent respectively.

[CCTA], [I], [M] and [solvent] are concentrations of initiator, monomer and solvent respectively.

DP_o = degree of polymerization in the absence of CCTA

Similarly,

$$\overline{DP} = \frac{Molecular\ weight\ of\ polymer\ chain}{Molecular\ weight\ of\ monomer\ repeat\ unit} \qquad (8)$$

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Identification of Complexes

Ultraviolet-visible spectroscopy was the first technique employed in characterizing the prepared complexes (sections 3.2.1 and 3.2.2). The UV-visible spectra obtained were distinctly different, as shown in figure 4.1 indicating that the two synthesis routes gave rise to different reaction products. Figure 4.1 (curve *a*) is the spectrum of the free ligand. Curve *b* in the same Figure, corresponds to the spectrum of complex A. The similarity in the two spectra suggests that cyclization did not occur, and that the required product did not form. However, the spectrum in Figure 4.1(curve *c*) is clearly different from the other two.

The absorption around 480 nm (in the visible region) in figure 4.1(curve *c*) is suggestive of an electronic transition in the cobalt atom. This value is close to that reported for the same complex in the literature [17]. Thus, the spectrum in figure 4.1(curve *c*) is undoubtedly, that of $Co(\alpha\text{-fdo-2H})_2(BF_2)_2{\cdot}2H_2O$. The decomposition temperature of the complex, found to be 303 ±1°C is also in good agreement with the value of 310°C quoted in the literature. Table 4.1 compares

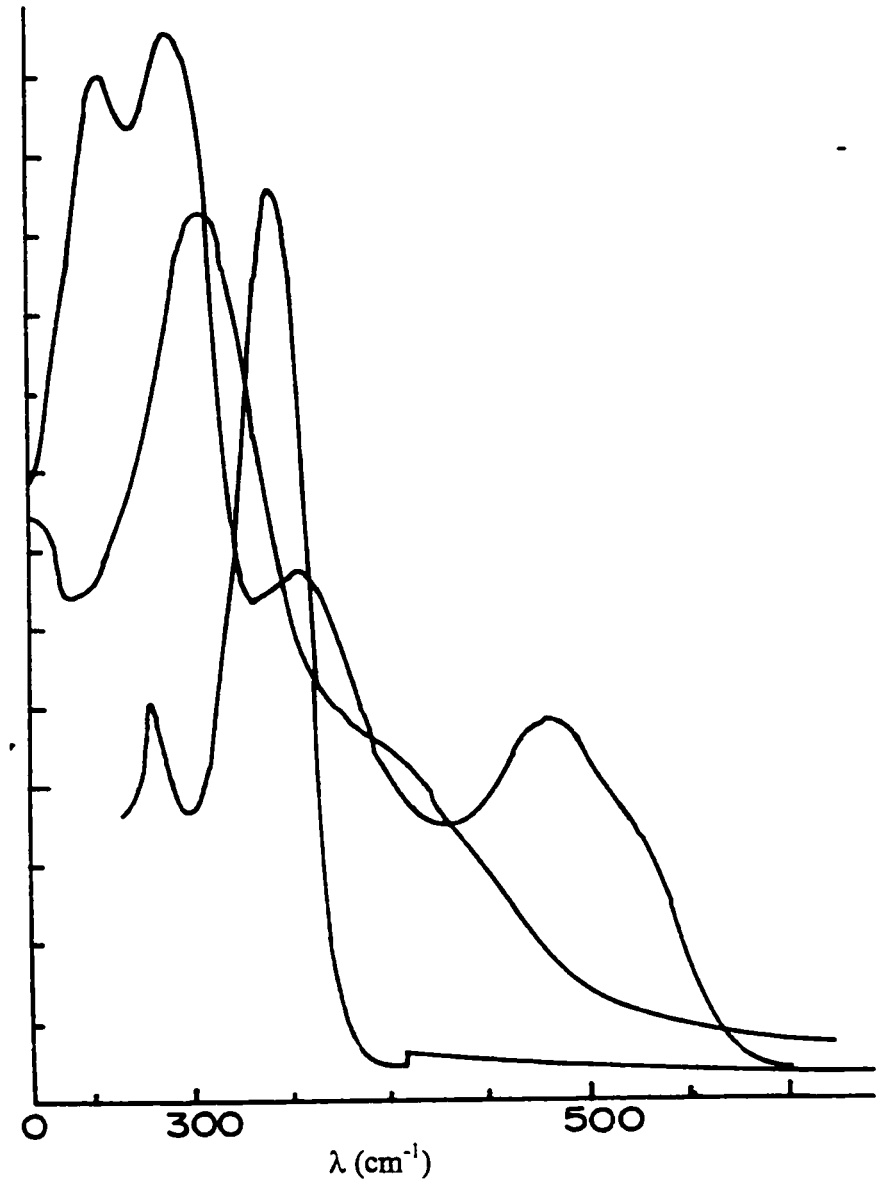


Figure 4.1 UV-visible Spectra of: (a) free ligand, (b) Complex prepared via hydrogen-bonded precursor, (c) Complex prepared by direct synthesis

UV-Visible data reported in the literature with those found experimentally for the complex [17].

Table 4.1 Ultraviolet-Visible Absorption Maxima for $Co(\alpha\text{-afdo-}2H)_2(BF_2)\bullet 2H_2O$

Parameter	Literature	Experimental
Absorption maxima (nm)		
Free ligand	270	266.9
Complex	285	288.1
Decomposition Temperature	310°C	303 ± 1°C

Based on the result of the absorption study, which suggests that complex B was closest to the expected product, elemental analysis was carried out on complex B alone. It was analyzed for carbon, nitrogen and hydrogen contents respectively. The experimental composition was found to agree favorably with the calculated composition, based on the calculated molecular weight of 628.89 for the formula $Co(\alpha\text{-fdo-}2H)_2(BF_2)_2{\cdot}2H_2O$ [17] as shown in Table 4.2. The results obtained were in good agreement, within the allowable limit of 3 - 4% of the expected values.

Table 4.2 Results of Elemental Studies on $Co(\alpha\text{-afdo-}2H)_2(BF_2)\bullet 2H_2O$

	% Element		
	Carbon	Nitrogen	Hydrogen
Calculated	38.20	8.55	2.56
Found	37.59	8.91	2.67

The infrared spectra of both the free ligand and the complex B are shown in figure 4.2 below. The two spectra show quite distinctive features in the hydroxyl absorption region. The absorption in this region in Figure 4.2(a) is broad suggesting extensive hydrogen bonding. However, the absorption of the complex in the same region (Figure 4.2(b)) is less broad, indicating less extensive hydrogen bonding. The hydroxyl absorption band observed in the spectra of the complex is likely to result from the two molecules of water that have been predicted from elemental analysis.

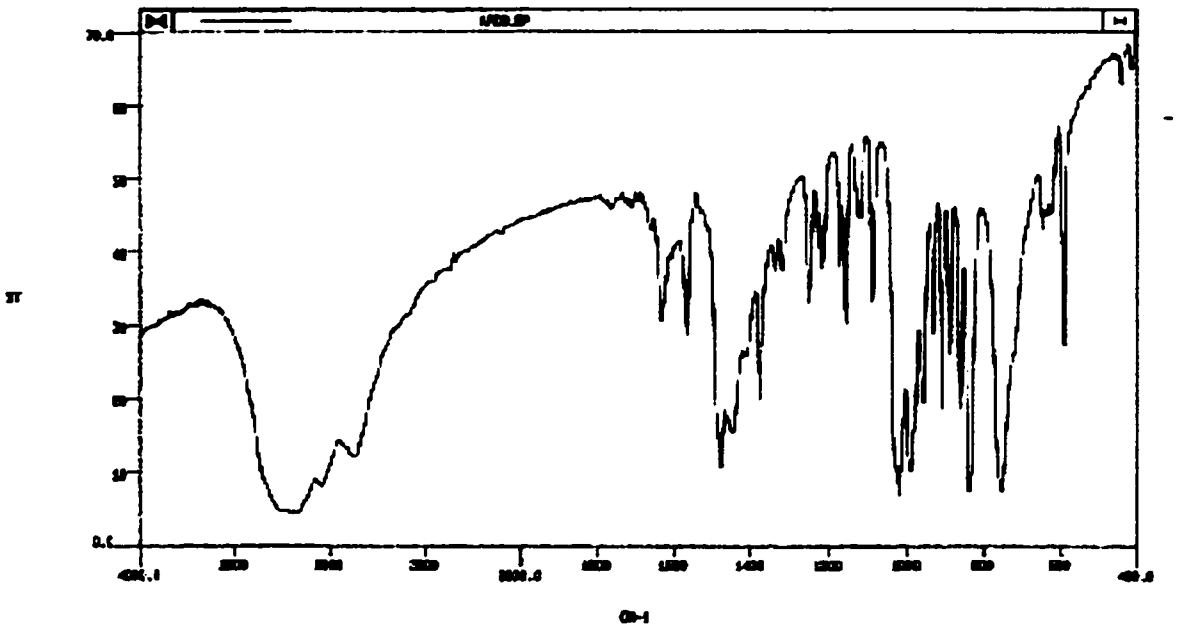


Figure 4.2a Infrared Spectrum of Alphafurilglyoxime

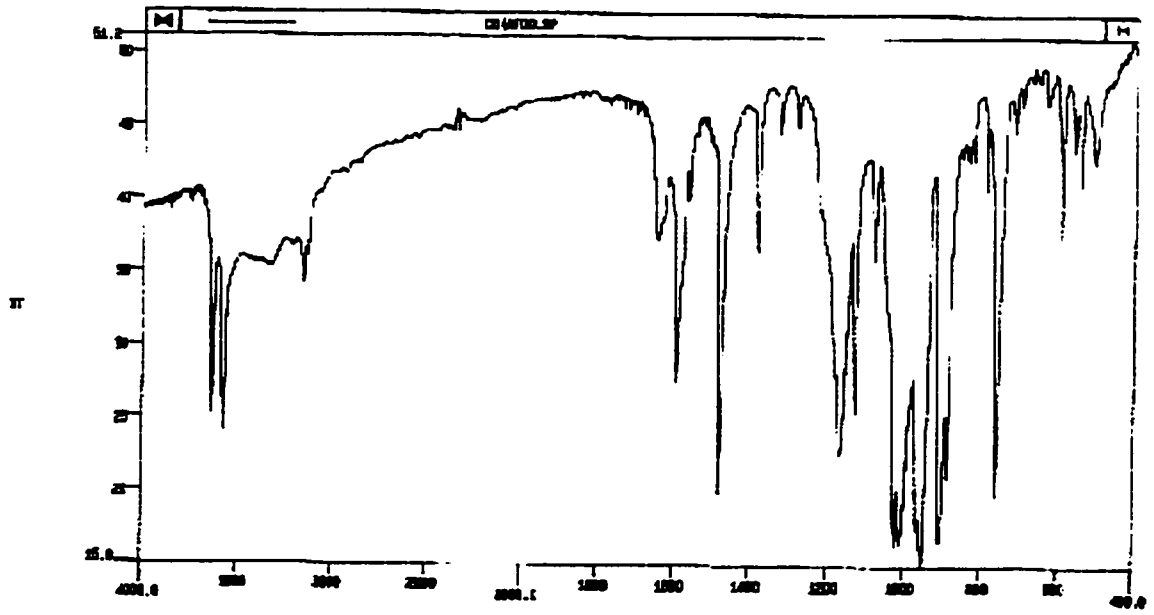


Figure 4.2b Infrared Spectrum of Cobalt (II) bis(dialphafurilglyoxime)

4.2 Molecular Weight of Polymer Samples from Screening Experiment

Poly(methyl methacrylate) samples obtained from the screening experiment in section 3.3.3 were analyzed by dilute solution viscometry (DSV). The viscosity average molecular weights, M_V of the samples were evaluated using the Mark-Houwink equation. Viscosity measurements were conducted at room temperature with chloroform as solvent. The relevant Mark-Houwink constants for the polymer-solvent pair were taken from Polymer Handbook [52, 53]. Molecular weight values of 630,364, 387,741 and 24,952 were obtained for the control experiment (no complex added), complex A (section 3.2.1) and complex B (section 3.2.2), respectively. Thus, addition of complex A decreased the molecular weight by a mere factor of 1.6. Whereas, the same amount of complex B decreased the molecular weight twenty five-fold. Clearly, complex B has shown higher catalytic chain transfer activity than complex A. It was therefore selected as the preferred CCTA that was studied in this work.

4.3 Effect of CCTA on Monomer Conversion

The experimental yield obtained from each system was evaluated from the masses of the polymer samples recovered after treating the samples according to the procedure in section 3.3.4. From these masses, monomer conversion to polymer was calculated. Comparison of the degree of conversion between the various

systems cannot be made satisfactorily, because certain experimental parameters had to be varied from one system to another. In case of styrene, temperature was raised to 76°C, before the effect of the CCTA could manifest. The temperature increase became necessary after obtaining low yield in the run made at 60°C. Even at 73°C, no tangible effect of the CCTA on molecular weight was observed. In other instances, it was difficult to maintain temperatures to ±1°C. It is well known that a 1°C change in temperature may result in significant changes in the kinetics of a free radical polymerization process, especially initiation.

Another parameter that was varied in the experimental setup was reaction time. It was important to allow ample time in order to obtain reasonable yield, maintaining low conversion at the same time. Again, the yield obtained with styrene at polymerization time used in methyl methacrylate system was very low. Thus reaction time for styrene was raised to three hours (3 hrs) before satisfactory yield was obtained. The concentration of the CCTA was relatively the same in all homopolymer systems, except for styrene, where the CCTA concentration had to be significantly increased, before any reasonable effect on the molecular weight could be observed. In the case of the copolymers systems, the CCTA concentration was kept constant.

A third reason why conversion cannot be readily compared is the possible influence of dissolved oxygen on the polymerization reactions. Even though great care and precaution were taken to ensure complete removal of as much air as possible by degassing, this could not be achieved 100 per cent, because the

monomers differed in viscosity. The more viscous monomer required more freeze-thaw cycles. For example, while methyl methacrylate required just five such cycles, 2-ethylhexyl methacrylate and the hydroxyl containing monomers required as many as ten cycles. Table 4.3 gives a summary of the monomer conversion as a function of CCTA concentration for all systems studied.

Table 4.3 Monomer Conversion as a function of CCTA Concentration (concentration increases down the columns).

	% Conversion							
Run #	PMMA	PBMA	Polystyrene (run one)	Polystyrene (run two)	PEHMA	MMA-co-BMA	Sty-co-MMA	Sty-co-BMA
Control	3.89	10.29	5.50	5.41	28.19	7.93	2.12	2.61
2	4.31	11.19	6.34	5.41	20.39	5.22	2.92	2.68
3	3.17	8.69	5.73	5.23	10.40	8.75	4.11	2.61
4	2.91	7.02	6.23	3.94	14.96	10.55	4.79	2.58
5	2.70	5.64	5.73	6.43	10.52	10.83	5.53	2.44
6	-	-	-	-	-	12.36	6.54	2.56

It can be seen from Table 4.3 that monomer conversion generally decreased with increasing CCTA concentration, for the homopolymers systems. This is in accord with trends reported in the literature [3, 9, 13, 38 and 43]. The decrease has been attributed to retardation in rate of polymerization brought about by the presence of the CCTA. The trend observed in the copolymer systems was however different.

A look at Table 4.3 also shows a generally higher conversion for 2-ethylhexyl methacrylate compared to the other methacrylate homopolymer systems. However, no pattern relating conversion to concentration of CCTA can be deduced. Since the duration of the reaction was the same for all three systems, a likely explanation to this observation could be reactivity difference. It is possible that the substituent, 2-ethylhexyl, has a greater influence on the stability of the monomer than the methyl or butyl substituent. However, steric factor would tend to predict a lower conversion than observed. Hence, the actual reason for the high conversion observed is not clear.

The copolymer systems involving styrene i.e. styrene-co-methyl methacrylate and styrene-co- butyl methacrylate gave low yields compared to the methyl methacrylate-co-butyl methacrylate system, even though the same monomer feed ratio, initiator and CCTA concentrations were used in all cases. A relatively constant trend in monomer conversion was in fact observed in the styrene-co-butyl methacrylate system. This observation and the longer reaction time required for the polymerization of styrene as earlier stated [16], could be

explained by the lower reactivity of styrene relative to the methacrylate monomers studied.

This reasoning could be explained in terms of the difference in polymerization kinetics for the monomers involved. A lower propagation rate constant K_p, has been reported for styrene compared to the methacrylate monomers [16]. Though styrene monomer is more reactive than the methacrylate monomers, the reverse is the case for the reactivity of the propagating radicals once initiation has taken place. This is because a substituent such as a phenyl ring increases the reactivity of the monomer by stabilizing it, thereby decreasing the reactivity of the corresponding radical [16]. That is, styrene propagates at a much slower rate than methyl methacrylate.

4.4 Characterization of Polymer Samples

Not much information was derived from the IR spectra of the polymer samples. ^{1}H-NMR spectra were taken in deuterated chloroform ($CDCl_3$). These spectra were obtained in order to aid in establishing the microstructure or tacticity of the polymer samples. The poly (methyl methacrylate) samples were found to be atactic, with the pendant methyl group randomly distributed on the chains, a characteristic of free radical systems. This suggests that the presence of the CCTA does not influence the microstructure of the resulting products, in line with literature reports. The NMR spectra of some of the samples showed absorption due to vinylic protons. Since all samples were rigorously cleaned to remove any

traces of monomer, this observation tends to support the proposed mechanism of catalytic chain transfer discussed in chapter one, which suggests the formation of chains with terminal unsaturation.

4.5 Molecular Weight of Polymer Samples

The molecular weights of the polymer samples were analyzed by two techniques, dilute solution viscometry (DSV) and gel permeation chromatography (GPC). In addition to number average molecular weight M_n, GPC also gives other molecular weight averages that enable the determination of polydispersity (PDI) of a polymer sample. The molecular weight obtained from DSV, referred to as viscosity average molecular weight M_V, is numerically different from the M_n obtained from GPC, because the two molecular weight averages are obtained by measurement of different properties of the polymer sample. The techniques are discussed separately below.

4.5.1 Molecular Weight from Dilute Solution Viscometry (DSV)

The plots of inherent viscosities of poly (methyl methacrylate) samples from section 3.3.6, obtained from the data in Table 4.4, are shown in Figure 4.3. The relative positions of these plots give an idea of the viscosity of the samples. The viscosity decreases on going from the first plot (control) down to the last in each

Figure. This decrease has a direct relation with molecular weight. The plots for the other systems are obtained from their corresponding data, and are given in Tables 4.5 – 4.11 and Figures 4.4 – 4.10, respectively. The intercepts of the plots with the vertical axis in the figures correspond to the limiting or intrinsic viscosities of the samples at infinite dilution. These intercepts are used in combination with the appropriate constants in the Mark-Houwink equation given in section 3.5.1 to evaluate the viscosity average molecular weight M_V.

Table 4.4 Viscometry Data for Poly (methyl methacrylate) Samples in Chloroform, taken at 25°C

	Inherent viscosity at different concentrations of CCTA $x10^6$ M				
Conc. of Polymer (g/dL)	(control) 0.00	(1) 0.51	(2) 1.08	(3) 1.88	(4) 4.41
0.5040	1.9879	0.4070	0.2006	0.1425	0.0867
0.4200	2.0483	0.4129	0.1945	0.1473	0.0870
0.3600	2.1056	0.4113	0.1995	0.1552	0.0873
0.3150	2.1079	0.4171	0.2091	0.1517	0.0932
0.2800	2.1119	0.4223	0.2067	0.1561	0.0974

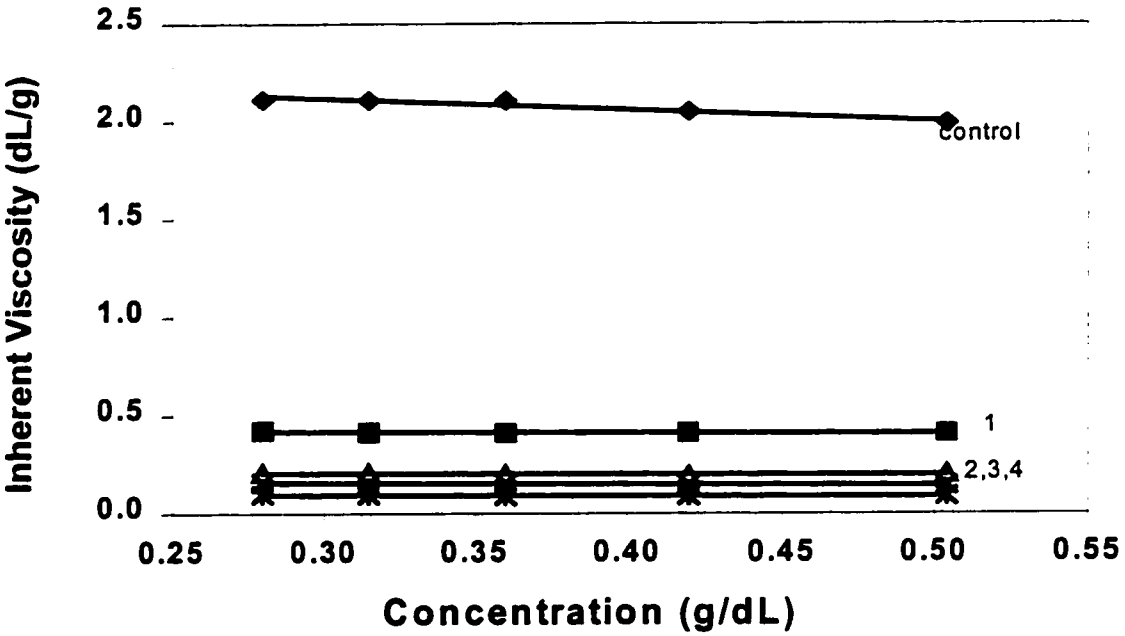


Figure 4.3 Plots of Inherent Viscosity of Poly (methyl methacrylate) Samples at different Concentrations of CCTA

Table 4.5 Viscometry Data for Poly (butyl methacrylate) Samples in Chloroform, taken at 25°C

	Reduced viscosity at different concentrations of CCTA x10^6 M				
Conc. of Polymer (g/dL)	(control) 0.00	(1) 0.76	(2) 1.51	(3) 2.25	(4) 2.98
0.5000	4.2785	1.0823	0.4971	0.3492	0.2607
0.3421	3.9157	1.0434	0.5034	0.3678	0.2326
0.2341	3.5035	0.9680	0.4283	0.3454	0.2137
0.1602	3.2501	0.9268	0.3983	0.3146	0.1912
0.1096	3.0585	0.9362	0.4069	0.3093	0.1720

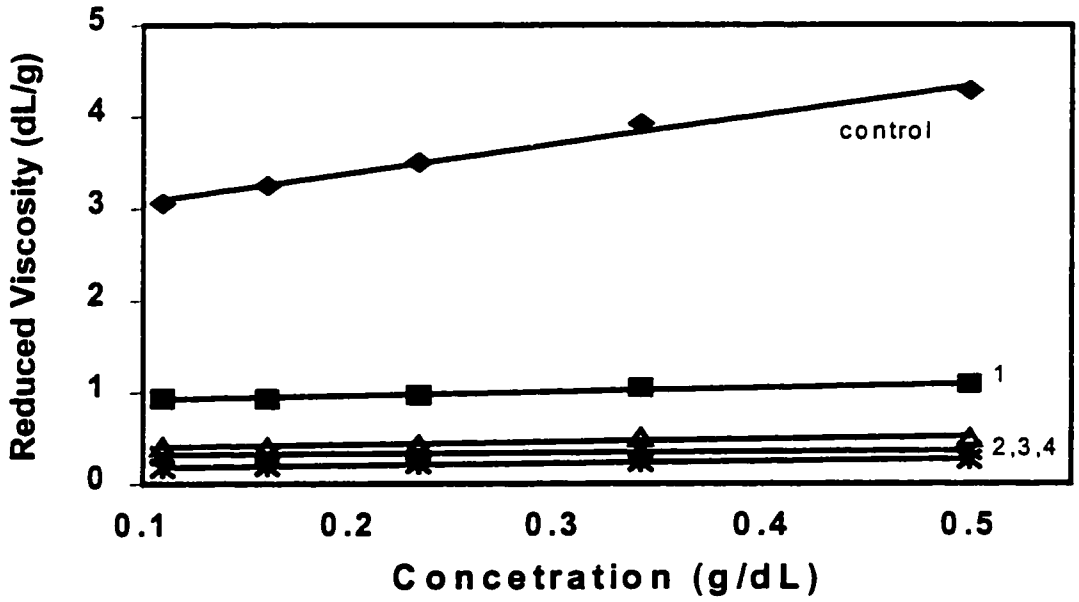


Figure 4.4 Plots of Reduced Viscosity of Poly (butyl methacrylate) Samples at different Concentrations of CCTA

Table 4.6 Viscometry Data for Polystyrene Samples in Chloroform, taken at 25°C (First run)

	Inherent viscosity at different concentrations of CCTA x10^6 M				
Conc. of Polymer (g/dL)	(control) 0.00	(1) 0.80	(2) 1.61	(3) 2.41	(4) 3.22
0.5000	0.5508	0.5151	0.5118	0.4653	0.5102
0.3636	0.5696	0.5242	0.5169	0.4731	0.5145
0.2857	0.5770	0.5327	0.5231	0.4780	0.5199
0.2353	0.5844	0.5409	0.5290	0.4850	0.5250
0.2000	0.5942	0.5469	0.5326	0.4895	0.5279

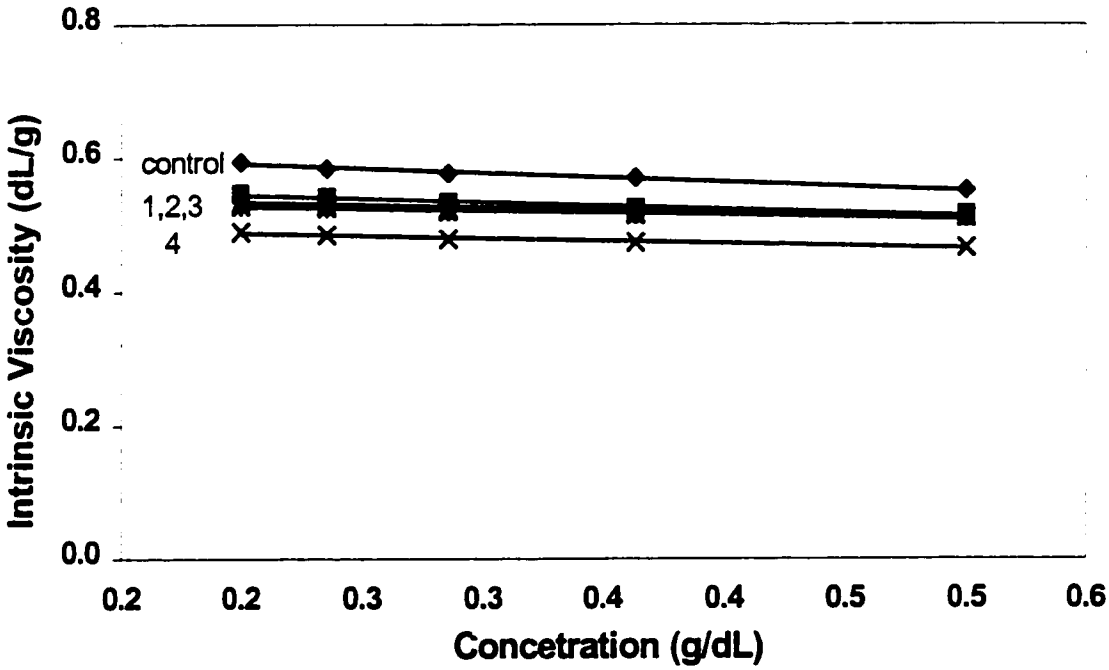


Figure 4.5 Plots of Inherent Viscosity of Polystyrene Samples at different Concentrations of CCTA (First run)

Table 4.7 Viscometry Data for Polystyrene Samples in Chloroform, taken at 25°C (second run)

	Inherent viscosity at different concentrations of CCTA x10^6 M				
Conc. of Polymer (g/dL)	(control) 0.00	(1) 3.74	(2) 7.35	(3) 14.1	(4) 17.4
1.0000	1.4978	0.9735	0.6814	0.5553	0.5243
0.7692	1.3921	0.9204	0.6558	0.5379	0.5148
0.6250	1.3381	0.8991	0.6301	0.5239	0.4920
0.5263	1.2989	0.8618	0.6095	0.5128	0.4750
0.4545	1.2802	0.8519	0.5939	0.5014	0.4673
0.4000	1.2168	0.8241	0.5918	0.4867	0.4591

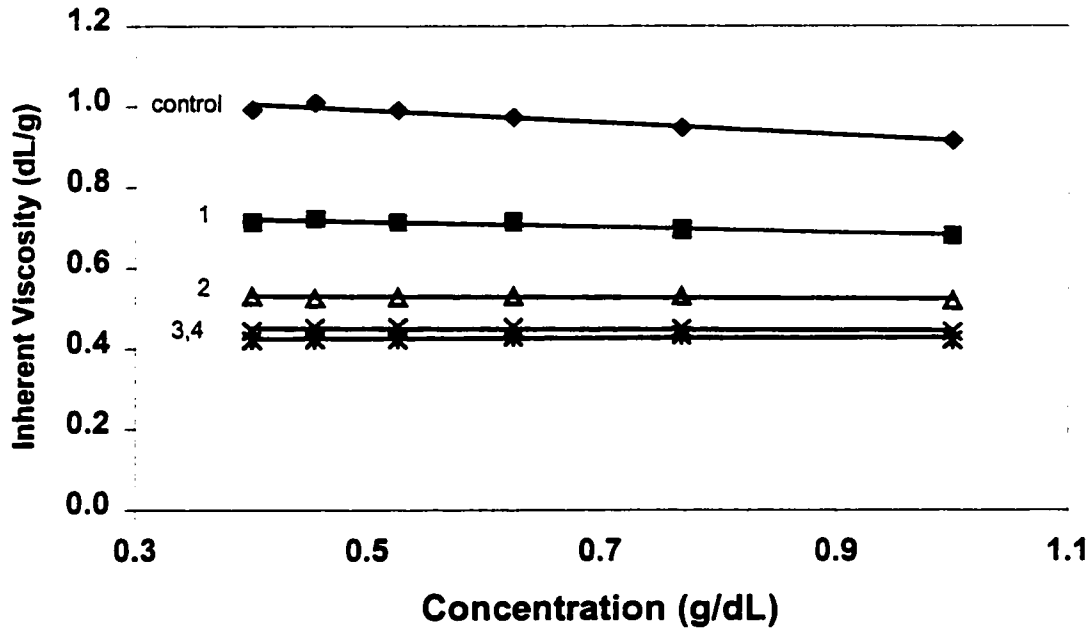


Figure 4.6 Plots of Inherent Viscosity of Polystyrene Samples at different Concentrations of CCTA (Second run)

Table 4.8 Viscometry Data for Poly (2-ethylhexyl methacrylate) Samples in Chloroform, taken at 25°C

	Reduced viscosity at different concentrations of CCTA x10^6 M				
Conc. of Polymer (g/dL)	(control) 0.00	(1) 0.81	(2) 1.61	(3) 3.22	(4) 4.12
1.0000	1.7249	0.9010	0.4340	0.3987	0.3417
0.7692	1.8743	0.9287	0.4382	0.3988	0.3487
0.6250	1.9355	0.9656	0.4422	0.4120	0.3512
0.5263	2.0151	0.9682	0.4446	0.3973	0.3562
0.4545	2.0789	0.9731	0.4486	0.4019	0.3583
0.4000	2.1004	0.9786	0.4500	0.4139	0.3588

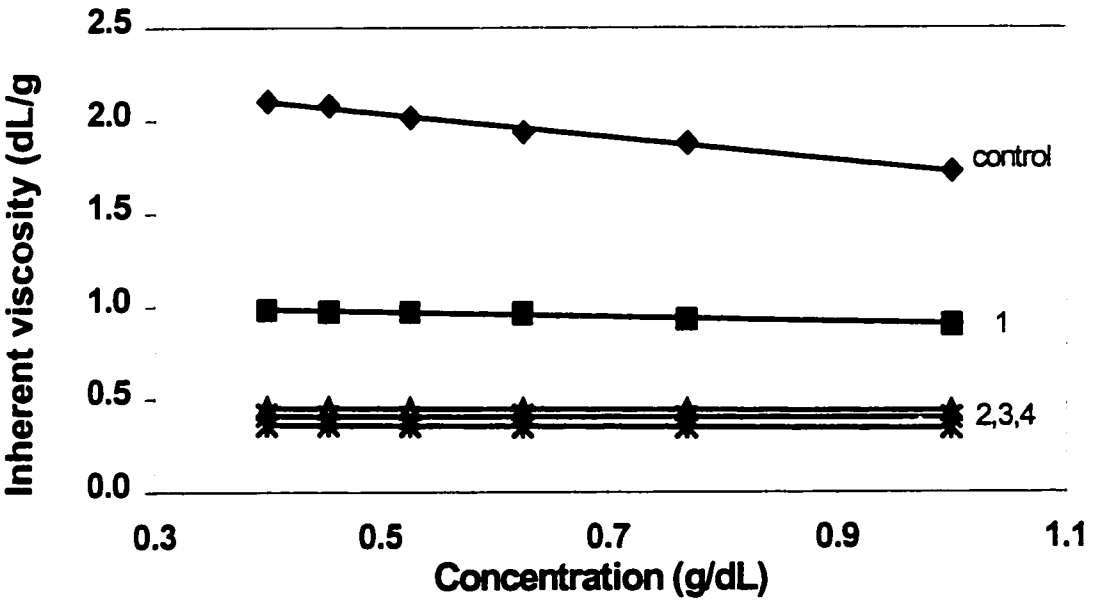


Figure 4.7 Plots of Inherent Viscosity of Poly (2-ethylhexyl methacrylate) Samples at different Concentrations of CCTA

Table 4.9 Viscometry Data for Poly (styrene-*co*-methyl methacrylate) Samples in Butanone, taken at 25°C

	Reduced viscosity at different concentrations of CCTA x10^6 M					
Conc. of Polymer (g/dL)	(control) 0.00	(1) 1.34	(2) 2.68	(3) 4.02	(4) 5.36	(5) 6.70
0.5682	0.7766	0.5192	0.4930	0.4201	0.3928	0.3689
0.4371	0.7620	0.5098	0.4827	0.4111	0.3837	0.3605
0.3551	0.7456	0.5023	0.4728	0.4037	0.3723	0.3523
0.2991	0.7365	0.4974	0.4663	0.3974	0.3674	0.3448
0.2583	0.7298	0.4922	0.4601	0.3934	0.3619	0.3423

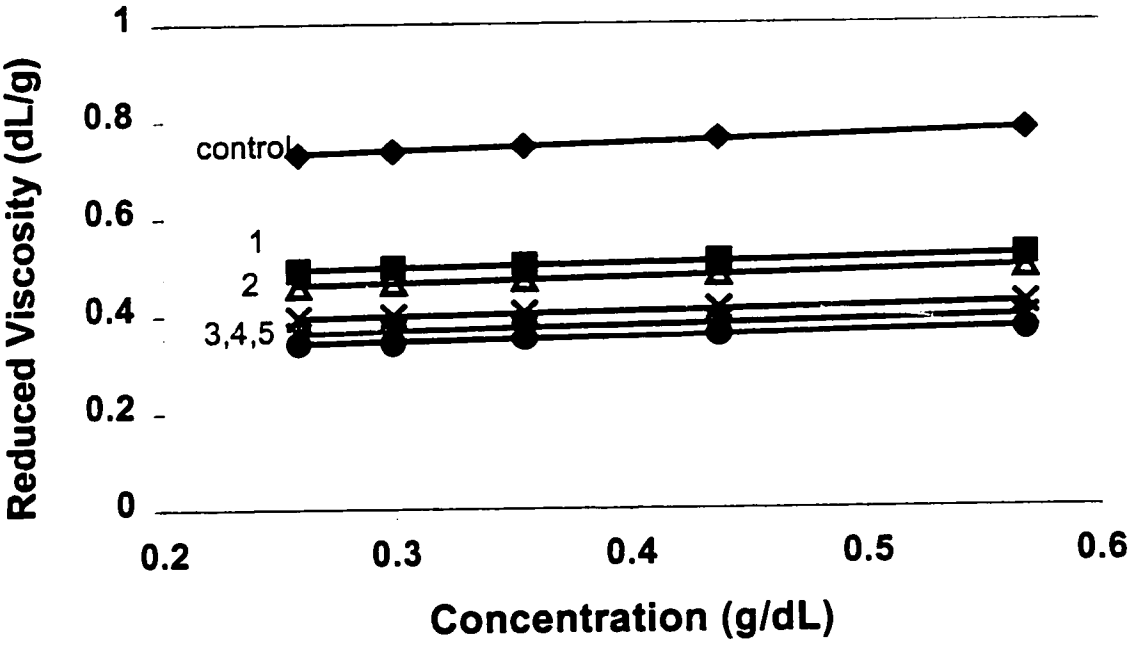


Figure 4.8 Plots of Reduced Viscosity of Poly (styrene-*co*-methyl methacrylate) Samples at different Concentrations of CCTA

Table 4.10 Viscometry Data for Poly (styrene-*co*-butyl methacrylate) Samples in Butanone, taken at 25°C

	Reduced viscosity at different concentrations of CCTA x10^6 M					
Conc. of Polymer (g/dL)	(control) 0.00	(1) 1.34	(2) 2.68	(3) 4.02	(4) 5.36	(5) 6.70
0.5682	0.8411	0.5292	0.4871	0.3620	0.3511	0.2716
0.4371	0.8218	0.5081	0.4706	0.3501	0.3279	0.2632
0.3551	0.7982	0.4883	0.4544	0.3367	0.3132	0.2552
0.2991	0.7872	0.4808	0.4372	0.3315	0.3075	0.2449
0.2583	0.7782	0.4713	0.4228	0.3218	0.2933	0.2395

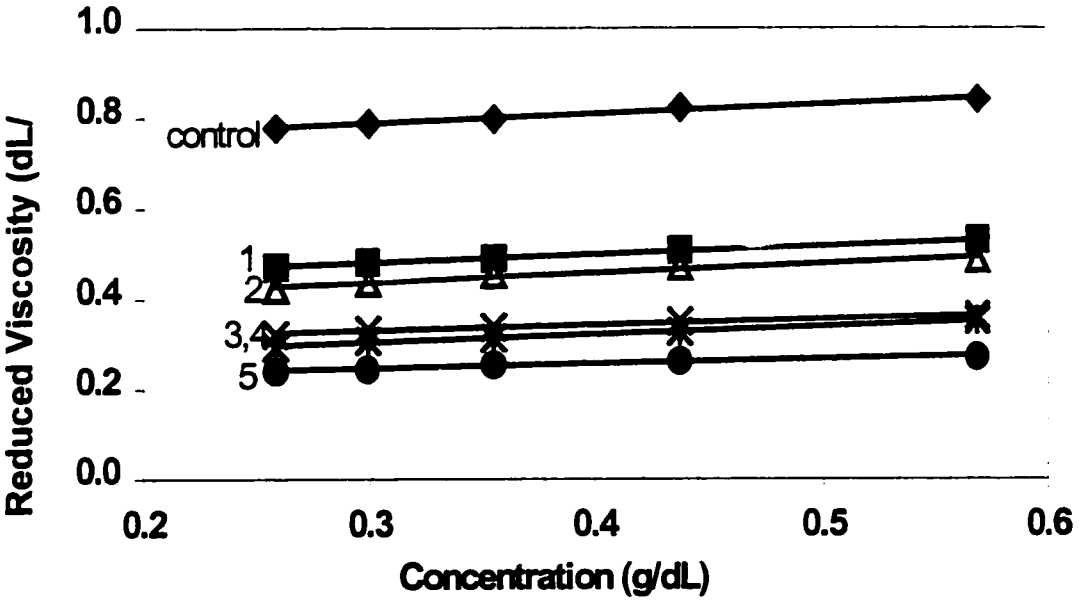


Figure 4.9 Plots of Reduced Viscosity of Poly (styrene-*co*-butyl methacrylate) Samples at different Concentrations of CCTA

Table 4.11 Viscometry Data for Poly (methyl methacrylate-*co*-butyl methacrylate) Samples in Butanone, at 25°C

	Reduced viscosity at different concentrations of CCTA x10^6 M					
Conc. of Polymer (g/dL)	(control) 0.00	(1) 1.34	(2) 2.68	(3) 4.02	(4) 5.36	(5) 6.70
0.5682	1.7456	0.6432	0.5872	0.3410	0.2582	0.2516
0.4371	1.6615	0.6387	0.5679	0.3383	0.2536	0.2497
0.3551	1.6082	0.6323	0.5613	0.3359	0.2511	0.2478
0.2991	1.5670	0.6262	0.5572	0.3349	0.2489	0.2461
0.2583	1.5309	0.6243	0.5522	0.3341	0.2470	0.2450

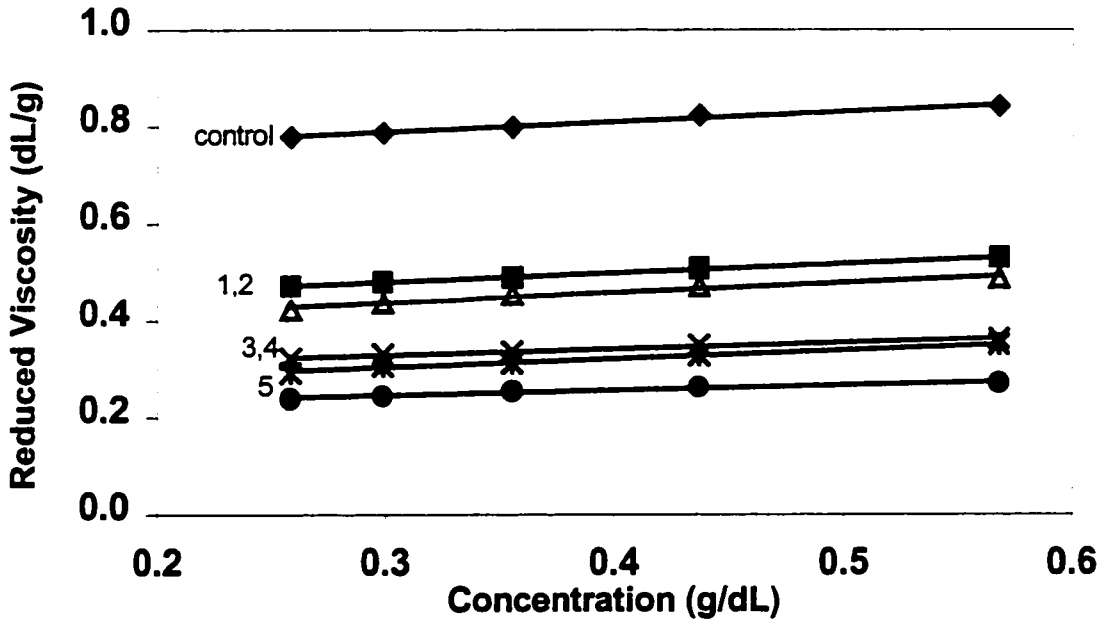


Figure 4.10 Plots of Reduced Viscosity of Poly (styrene-*co*-butyl methacrylate) Samples at different Concentrations of CCTA

The viscosity average molecular weight, M_V of all samples was found to decrease with increasing CCTA concentration The results agrees with data from studies carried out on similar systems published in the literature [3, 9, 13]. The decrease however varied widely from one system to another. The most dramatic change on going from the control sample (no CCTA) to the first sample containing the smallest amount of the CCTA (5.05×10^{-7} M) in the homopolymer series was observed with the methacrylates, particularly methyl methacrylate. Styrene did not show as much change in molecular weight. The decrease became less pronounced at higher concentrations of the CCTA, with poly (methyl methacrylate) showing the least sensitivity to increase in CCTA concentration.

A look at the molecular weights corresponding to the control samples (no CCTA) for the homopolymer systems shows a much larger magnitude for the methacrylate systems compared to polystyrene. This could also be explained by difference in reactivity as has been discussed earlier in section 4.3. In the case of polystyrene, the molecular weights of samples in the first run (section 3.3.12) were lower than those obtained in the second run (section 3.3.13). Though, the yields in both cases did not differ greatly. However, reaction time in the second run was double that in the first run. The longer reaction time is supposed to result in higher monomer conversion. At the same time however, the presence of high concentration of the CCTA may cause substantial retardation in the rate of propagation as already discussed. This may offset the effect of increased reaction time. The copolymers involving styrene had lower molecular weights compared

to the methyl methacrylate-co-butyl methacrylate system. In this case, reaction time, initiator and CCTA concentrations were the same. This further suggests that different reaction kinetics is involved in the two cases, and monomer reactivity also plays an important role. However, in all the systems, a general trend of decreasing molecular weight with increasing CCTA concentration was observed. Again, correlation cannot be made between the systems.

It is important to note that dilute solution viscometry is a secondary method of determining molecular weight. Therefore, the technique is likely to have some shortcomings. First, the use of a manual stopwatch in measuring the flow time past the viscometer marks is likely to introduce some error in the evaluation of relative viscosity. This would certainly affect subsequent calculations in which the relative viscosities are used. Secondly, the Mark-Houwink constants used in the analysis are themselves approximations. This is so because the experimental conditions under which they were determined originally cannot be reproduced exactly in the laboratory. These include solvent purity, temperature, concentration, cannot be matched exactly.

Thirdly, viscometry technique does not give a direct relation between the absolute viscosity of a polymer solution and the polymer molecular weight, because the two constants in the Mark-Houwink equation have to be determined using primary methods such as light scattering, sedimentation, vapor pressure osimometry, etc in a separate experiment. The constants so determined may also yield different values for the same polymer-solvent pair, depending on which

method was used to determine them. Table 4.12 gives molecular weight as a function of CCTA concentration for all the systems studied.

Table 4.12 Variation of Viscosity Average Molecular Weight with CCTA Concentration for all Systems (Obtained from Dilute Solution Viscometry)

	Viscosity Average Molecular Weight, M_v							
Run #	PMMA	PBMA	Polystyrene (run one)	Polystyrene (run two)	PEHMA	MMA-co-BMA	Sty-co-MMA	Sty-co-BMA
Control	699,857	884,073	151,121	308,873	728,448	941,714	257,166	260,663
2	89,822	212,270	134,249	190,846	262,048	307,925	145,874	129,621
3	39,823	72,056	127,909	122,499	94,150	249,780	129,362	111,223
4	28,209	65,269	115,213	99,894	83,043	130,608	102,693	79,847
5	16,199	24,382	125,935	89,858	72,471	83,719	88,779	65,521
6	-	-	-	-	-	84,501	82,073	53,726

4.5.2 Molecular Weight from Gel Permeation Chromatography (GPC)

Several molecular weight averages are obtainable from gel permeation chromatography, the number average molecular weight (M_n) being one of them. It is numerically different from viscosity average molecular weight M_V, obtained from dilute solution viscometry. As mentioned earlier, they are determined by different techniques such as light scattering, sedimentation, vapor pressure osimometry and viscometry. Since these techniques measure different properties, the two molecular weight averages cannot be compared numerically. The microstructure of the standards used in the literature may also differ from that of the samples under study. This may render the Mark-Houwink constants to become mere approximations. It may also make the samples to exhibit rheological behavior in solution different from that of the standards. Other molecular weight averages obtainable from GPC include weight average molecular weight M_W and Z average molecular weight M_Z. The ratio of the weight average molecular weight to the number average molecular weight gives the polydispersity of a polymer sample. Table 4.13 gives the number average molecular weight values for the systems studied.

The molecular weights of poly(methyl methacrylate) samples were observed to be the lowest in the series of homopolymers studied. The control sample had the highest value of 63,868, while the lowest value of 5,258 was obtained for the sample containing 4.41×10^{-6} M CCTA. It should be noted that

Table 4.13 Variation of Number Average Molecular Weight (Obtained from Gel Permeation Chromatography) with CCTA Concentration for all Systems

	Number Average Molecular Weight , M_n				
Run #	PMMA	PBMA	Polystyrene (run one)	Polystyrene (run two)	PEHMA
Control	63,868	147,177	259,950	535,810	93,144
2	13,071	66,735	332,433	236,318	81,140
3	8,547	23,712	273,407	144,082	61,183
4	5,540	19,717	308,537	68,096	42,055
5	5,258	15,139	220,903	44,857	37,527

polystyrene standards were used to calibrate the GPC columns, in the absence of poly(methyl methacrylate) or universal standards. Running poly(methyl methacrylate) samples calibrated columns with a different standard may not give the same results as would columns calibrated with the right standard. Difference in size may influence the interaction between the stationary phase in the column and the sample molecules, since molecular size is inversely proportional to elution time. This will translate into lower molecular weights for the poly(methyl methacrylate) samples.

A comparison of poly(butyl methacrylate) and poly(2-ethylhexyl methacrylate) shows that except for the control sample, the latter gave samples of higher molecular weight than the former. Following the reasoning outlined above, this behavior is expected, because 2-ethylhexyl methacrylate has larger molecular size than butyl methacrylate. Variation of molecular weight with CCTA concentration was similarly found to be less with 2-ethylhexyl methacrylate. When polystyrene samples from the first run are compared with those from the second run, we see a higher molecular weight in the latter. This is unexpected, because in general, the molecular weight of samples produced in a free radical-initiated polymerization reaction are independent of the time of reaction [16].

However, since the temperature of the reaction was also raised to 76°C from 73°C, one can expect a change in the rate of initiation and possibly propagation. Therefore, an increase in molecular weight as observed may only be justified by supposing that increase in concentration of the CCTA did not increase

its chain transfer efficiency in the styrene system, due to the absence of an alpha methyl substituent as suggested in the literature [43].

4.6 Catalytic Chain Transfer Constant, C_S

Catalytic chain transfer constant is obtained from the slope of the Mayo plot. The Mayo equation given in section 3.5.2 can be rearranged to yield a straight-line plot with zero intercept. However, the plots obtained did not pass through the origin because the second term in the equation consists of several variables that play significant role in the kinetics of the polymerization reaction. For example initiator efficiency, rate of propagation and termination (by combination or disproportionation) and chain transfer to monomer, solvent and initiator, etc. The catalytic chain transfer constants obtained by the (DSV and GPC) are separately discussed below.

4.6.1 Catalytic Chain Transfer Constant from Dilute Solution Viscometry (DSV)

The Mayo plots for molecular weight determination are shown in Figures 4.12 – 4.17. The catalytic chain transfer constant (C_S) values obtained from these plots are given in Table 4.20. As a result of the higher molecular weight values encountered with dilute solution viscometry, relatively lower C_S values were obtained. The highest value of 14,411 was obtained with methyl methacrylate, followed by butyl methacrylate with 12,361. Polystyrene gave the lowest C_S value of 103. This value is in the range of that reported with cobalt dimethylglyoxime [43]. The reason given for the low value was the absence of an alpha methyl

group from which the hydrogen can be abstracted as postulated by the generally accepted mechanism discussed in chapter one. However, it is to be noted that no reports are available in the literature on the use of dilute solution viscometry to determine C_S. Rather, all the reports are based on the use of gel permeation chromatography. In the case of methyl methacrylate and butyl methacrylate, the values fall within the range reported for patented CCTAs. A value of 3,083 was recorded for 2-ethylhexyl methacrylate.

For the copolymer systems, no literature values are available, therefore, a comparison of the efficiency of the CCTA in these systems cannot be made. The values are however quite low, especially for the styrene-methyl methacrylate system where the value was only 720. The other systems gave values of 1,433 and 1,259 respectively.

Table 4.14 Degree of Polymerization for Poly (methyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] x10^6 $molL^{-1}$	M_v	DP	1/DP x 10^3	[1/DP-1/DP_o] x 10^3	[S]/[MMA] x 10^7
0.00	699,857	6,985	0.14	0.00	0.00
0.51	89,822	896	1.12	0.98	0.54
1.08	39,823	397	2.52	2.38	1.15
1.88	28,209	282	3.55	3.41	2.00
3.94	16,199	162	6.19	6.05	4.18

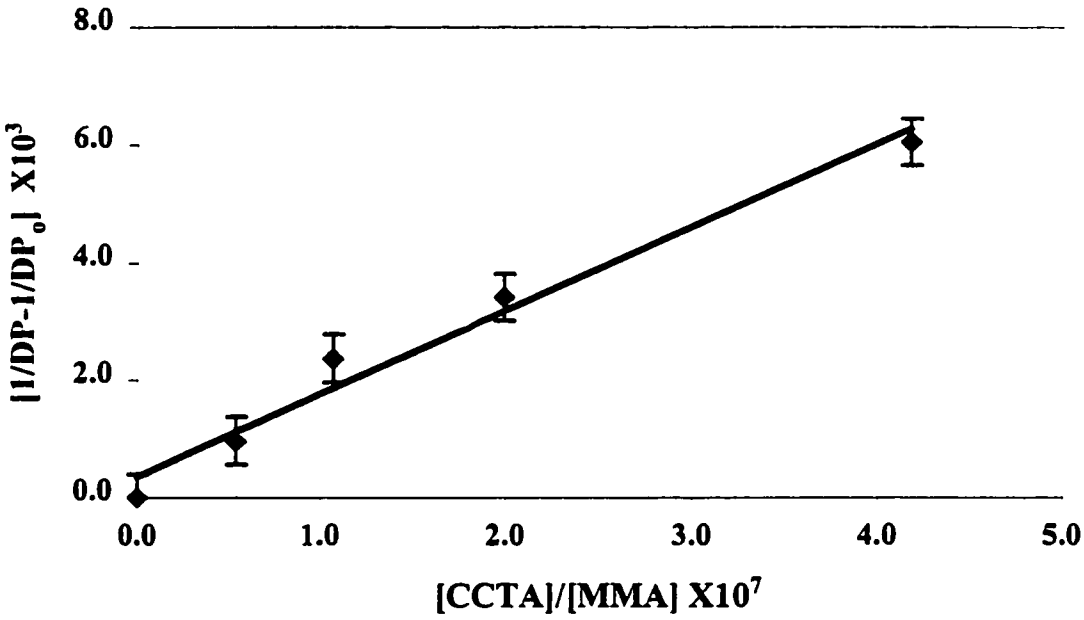


Figure 4.11 Mayo (regression) Plot for the Determination of Cs Value Poly (methyl methacrylate) samples from Dilute Solution Viscometry

Table 4.15 Degree of Polymerization for Poly (butyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] x10^6 $molL^{-1}$	M_v	DP	1/DP x 10^3	[1/DP-1/DP_o] x 10^3	[S]/[BMA] x 10^7
0.00	884,073	6,217	0.16	0.00	0.00
0.76	212,270	1,493	0.67	0.51	1.20
1.51	72,056	507	1.97	1.81	3.39
2.25	65,269	459	2.18	2.02	3.59
2.98	24,382	171	5.83	5.67	4.72

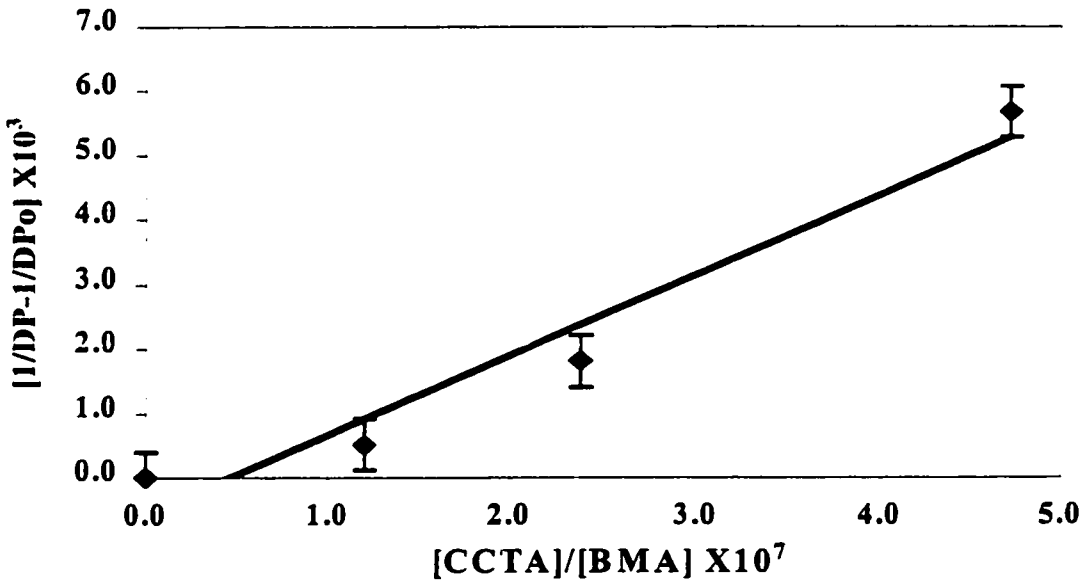


Figure 4.12 Mayo (regression) Plot for the Determination of Cs Value Poly (butyl methacrylate) samples from Dilute Solution Viscometry

Table 4.16 Degree of Polymerization for Polystyrene samples from Dilute Solution Viscometry

[CCTA] $x10^6$ $molL^{-1}$	M_v	DP	1/DP $x\ 10^4$	$[1/DP-1/DP_o]$ $x\ 10^4$	[S]/[Sty] $x10^7$
0.00	308,873	2,956	3.38	0.00	0.00
3.75	190,846	1,826	5.48	2.10	4.31
7.35	122,499	1,172	8.53	5.15	8.47
14.10	99,894	956	10.46	7.08	16.24
17.40	89,858	860	11.63	8.25	20.05

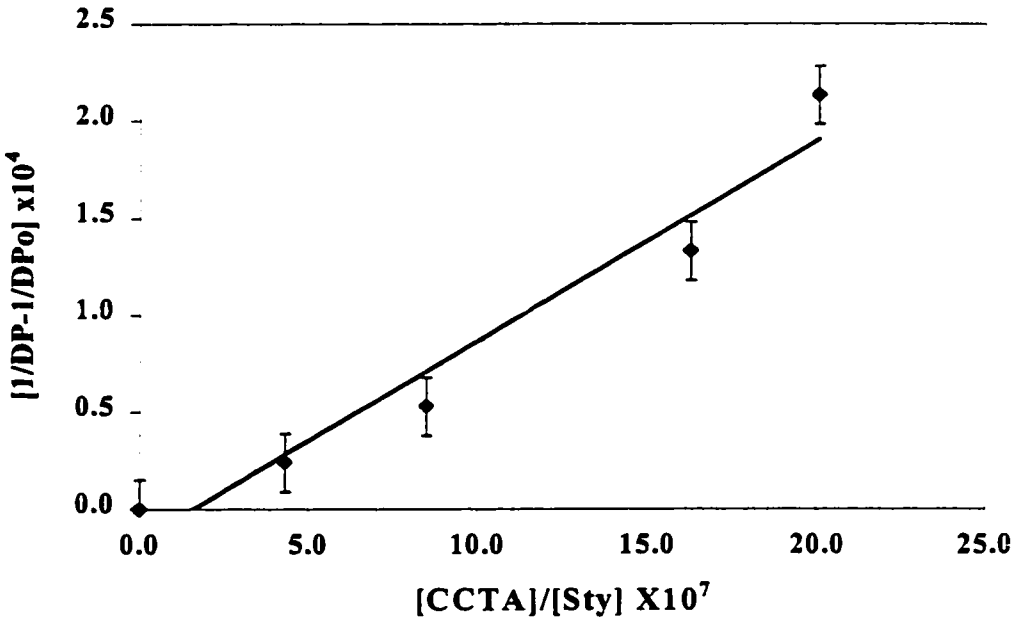


Figure 4.13 Mayo (regression) Plot for the Determination of Cs Value Polystyrene samples from Dilute Solution Viscometry

Table 4.17 Degree of Polymerization for Poly (2-Ethylhexyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] $x10^6$ $molL^{-1}$	M_v	DP	1/DP $x\ 10^4$	$[1/DP-1/DP_o]$ $x\ 10^4$	[S]/[EHMA] $x10^7$
0.00	728,448	1,558	0.64	0.00	0.00
0.76	262,048	962	1.04	0.40	1.70
2.25	94,150	618	1.62	0.98	5.56
2.98	83,043	504	1.99	1.35	6.70
3.70	72,471	453	2.21	1.57	8.31

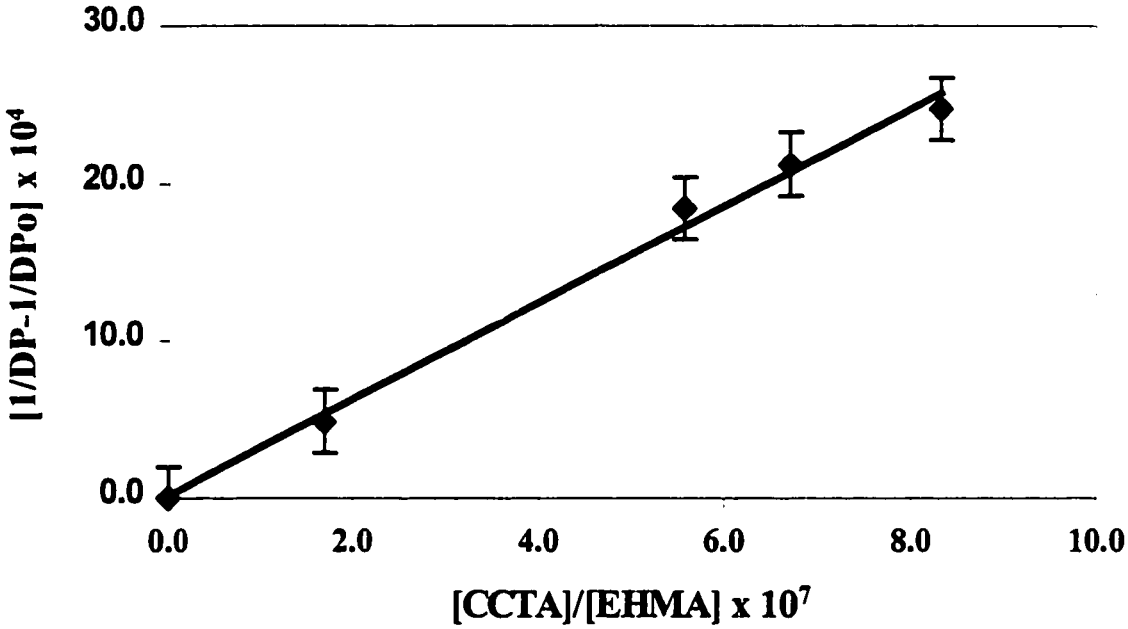


Figure 4.14 Mayo (regression) Plot for the Determination of Cs Value Poly (2-ethylhexyl methacrylate) samples from Dilute Solution Viscometry

Table 4.18 Degree of Polymerization for Poly (methyl methacrylate-co-butyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] $x10^6$ $molL^{-1}$	M_v	DP	1/DP $x\ 10^3$	$[1/DP-1/DP_o]$ $x\ 10^3$	[S]/[M-co-B] $x10^7$
0.00	941,714	6,622	0.15	0.00	0.00
2.24	307,925	2,165	0.48	0.31	2.85
4.36	249,780	1,757	0.57	0.42	5.55
6.48	130,608	918	1.09	0.94	8.25
8.58	83,719	589	1.70	1.55	10.93
10.60	84,501	594	1.68	1.53	13.50

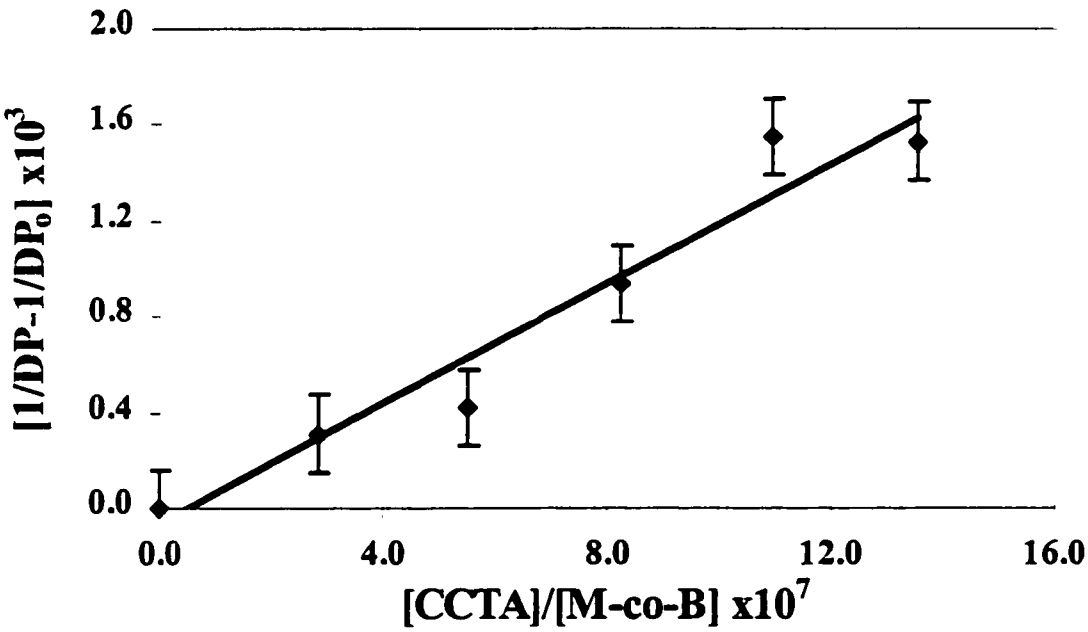


Figure 4.15 Mayo (regression) Plot for the Determination of Cs Value Poly (methyl methacrylate-co-butyl methacrylate) samples from Dilute Solution Viscometry

Table 4.19 Degree of Polymerization for Poly (styrene-co-methyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] $x10^6$ $molL^{-1}$	M_v	DP	1/DP $x\ 10^3$	$[1/DP-1/DP_o]$ $x\ 10^3$	[S]/[Sty-co-B] $x10^7$
0.00	257,166	2,461	0.41	0.00	0.00
2.24	145,874	1,396	0.72	0.31	2.47
4.36	129,362	1,238	0.81	0.40	4.82
6.48	102,693	983	1.02	0.61	7.16
8.58	88,779	850	1.18	0.77	9.48
10.60	82,073	785	1.27	0.86	11.71

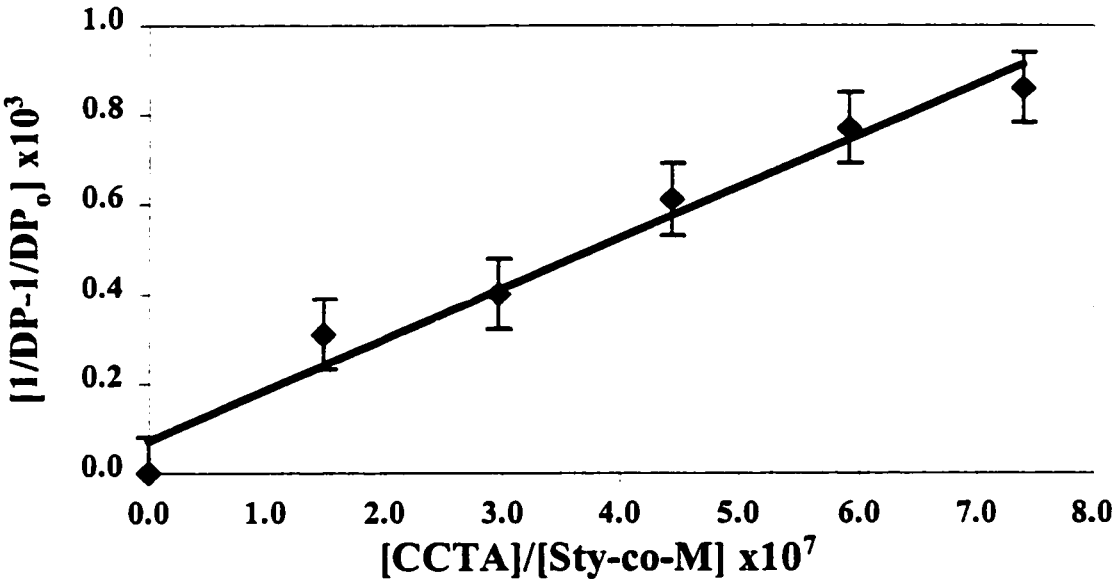


Figure 4.16 Mayo (regression) Plot for the Determination of Cs Value Poly (styrene-co-methyl methacrylate) samples from Dilute Solution Viscometry

Table 4.20 Degree of Polymerization for Poly (styrene-co-butyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] $x10^6$ $molL^{-1}$	M_v	DP	1/DP $x\ 10^3$	$[1/DP-1/DP_o]$ $x\ 10^3$	[S]/[Sty-co-B] $x10^7$
0.00	260,663	1,833	0.55	0.00	0.00
2.24	129,621	912	1.1	0.55	2.47
4.36	111,223	782	1.28	0.73	4.82
6.48	79,847	562	1.78	1.23	7.16
8.58	65,521	461	2.17	1.62	9.48
10.60	53,726	378	2.65	2.1	11.71

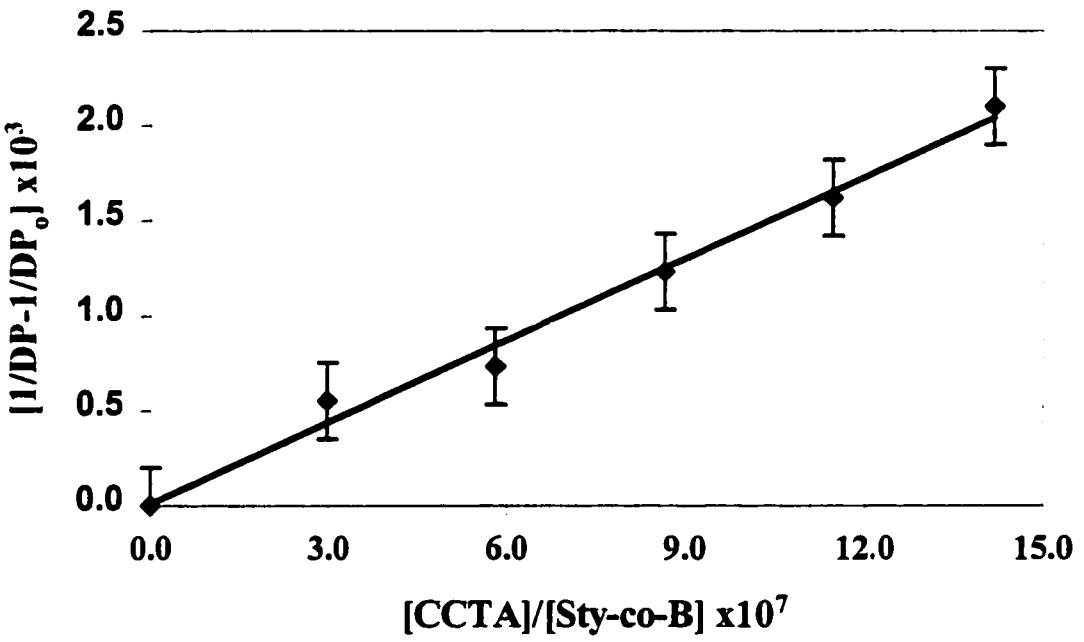


Figure 4.17 Mayo (regression) Plot for the Determination of Cs Value Poly (styrene-co-butyl methacrylate) samples from Dilute Solution Viscometry

Table 4.21 Catalytic Chain Transfer Constant (C_S) Values from Dilute Solution Viscometry (DSV)

Monomer	C_S Value
Methyl methacrylate	14,411
Butyl methacrylate	12,361
Polystyrene	103
2-Ethylhexyl methacrylate	3,083
Styrene-co-methyl methacrylate	720
Styrene-co-butyl methacrylate	1,433
Methyl methacryiate-co-butyl methacrylate	1,259

4.6.2 Catalytic Chain Transfer Constant from Gel Permeation Chromatography (GPC)

Gel permeation chromatography is the standard method of molecular analysis from which catalytic chain transfer constant C_S is evaluated. All C_S values reported in the literature are based on this method of molecular weight analysis. Therefore, the C_S values calculated from dilute solution viscometry are not comparable to those obtained from GPC. The factors listed earlier that may introduce error in molecular weight determination will similarly affect the C_S value because C_S is dependent on molecular weight.

The highest C_S value of 81,258 was recorded for methyl methacrylate. This value is even greater than the highest value (40,000) reported for DuPont patented cobalt dimethylglyoxime. The CCTA studied yielded a value of 18,532 for butyl methacrylate, which is quite reasonable, though there is no literature results to compare with. Next came 2-ethylhexyl methacrylate with 3,886, while styrene gave the lowest value of 1,035. This trend is same as that observed with C_S values obtained from dilute solution viscometry. In general, it can be said that the CCTA shows more sensitivity towards methacrylate monomers than styrene. This is also evident in the literature, as only few workers have conducted and reported catalytic chain transfer studies using styrene. This may not be unconnected to the low response of styrene to the CCTA, due to the absence of an alpha methyl substituent as proposed in the literature [43].

Table 4.22 Degree of Polymerization for Poly(methyl methacrylate) samples from Gel Permeation Chromatography (GPC)

[CCTA] x10^6 $molL^{-1}$	M_v	DP	1/DP x 10^3	[1/DP-1/DP_o] x 10^3	[S]/[MMA] x 10^7
0.00	63,868	637	1.57	0.00	0.00
0.51	13,071	130	7.67	6.10	0.54
1.08	8,547	85	11.72	10.15	1.15
1.88	5,540	55	18.09	16.52	2.00
4.41	5,258	52	19.06	17.49	4.68

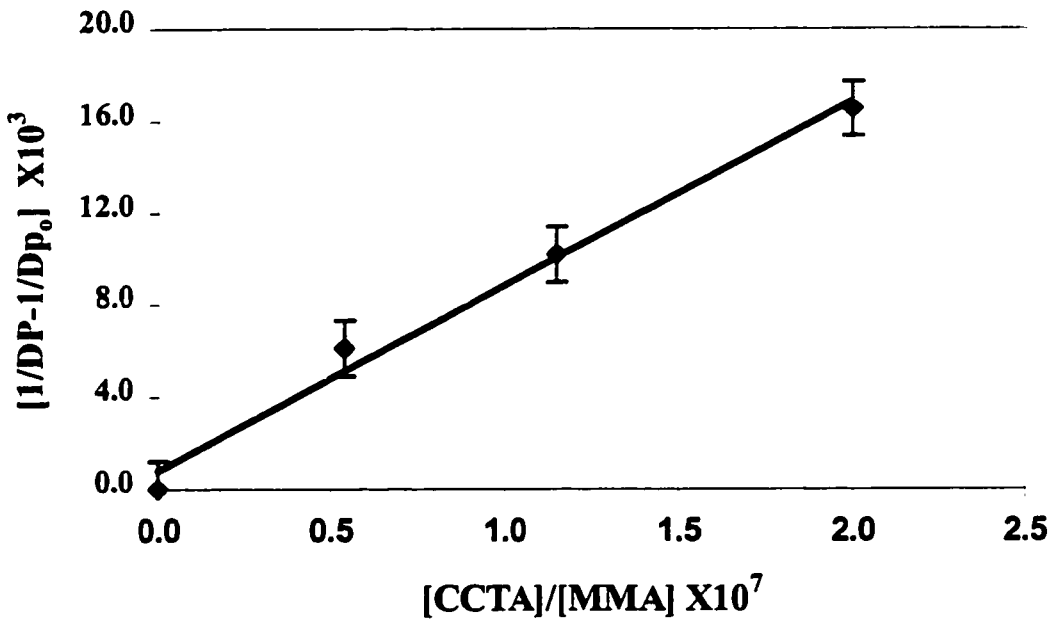


Figure 4.18 Mayo (regression) Plot for the Determination of Cs Value Poly(methyl methacrylate) samples Gel Permeation Chromatography (GPC)

Table 4.23 Degree of Polymerization for Poly(butyl methacrylate) samples from Gel Permeation Chromatography (GPC)

[CCTA] x10^6 $molL^{-1}$	M_v	DP	1/DP x 10^3	[1/DP-1/DP_o] x 10^3	[S]/[BMA] x 10^7
0.00	147,177	1,035	0.97	0.00	0.00
0.76	66,735	469	2.13	1.16	1.20
1.51	23,712	167	5.99	5.02	3.39
2.25	19,717	139	7.21	6.24	3.59
2.98	15,139	106	9.39	8.42	4.72

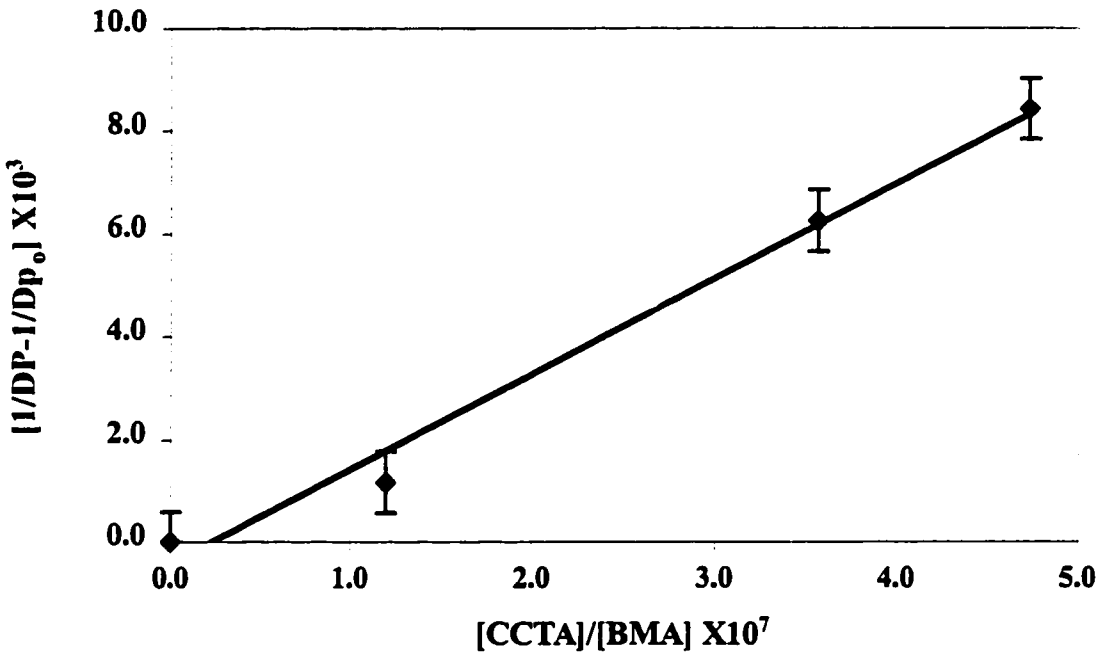


Figure 4.19 Mayo (regression) Plot for the Determination of Cs Value Poly(butyl methacrylate) samples Gel Permeation Chromatography (GPC)

Table 4.24 Degree of Polymerization for Polystyrene samples from Gel Permeation Chromatography (GPC)

[CCTA] x10^6 $molL^{-1}$	M_v	DP	1/DP x 10^4	[1/DP-1/DP_o] x 10^4	[S]/[Sty] x 10^7
0.00	535,810	5,127	1.95	0.00	0.00
3.75	236,318	2,261	4.42	2.47	4.31
7.35	144,082	1,379	7.25	5.30	8.47
14.10	68,096	652	15.34	13.39	16.24
17.40	44,857	429	23.31	21.36	20.05

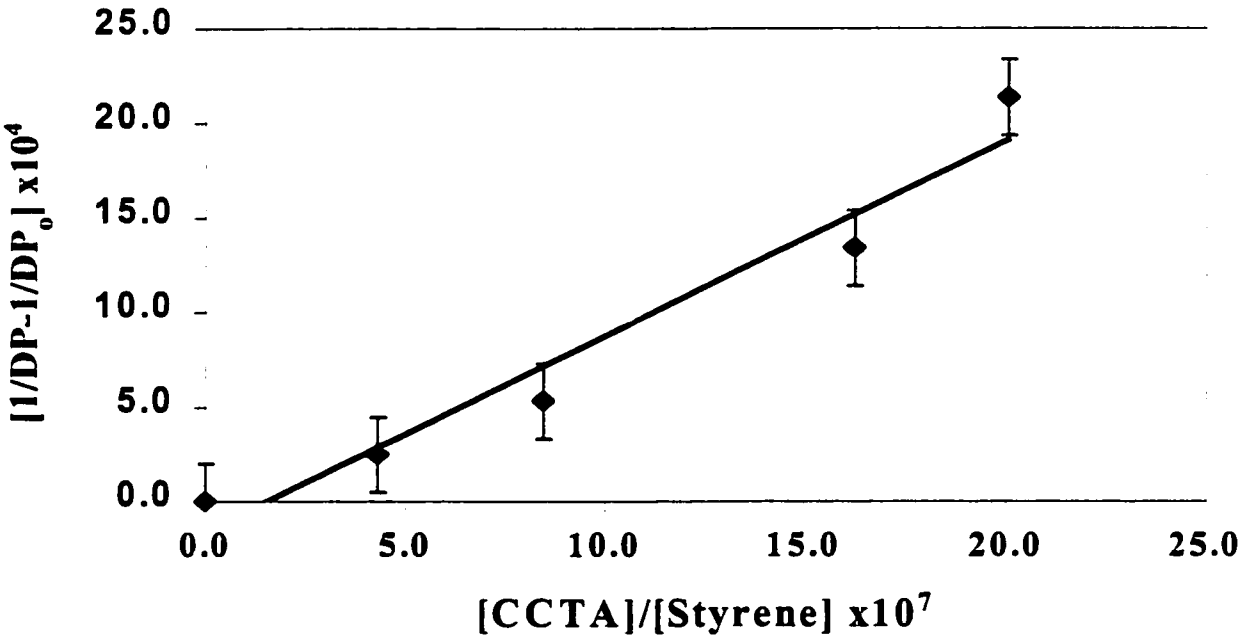


Figure 4.20 Mayo (regression) Plot for the Determination of Cs Value Polystyrene samples Gel Permeation Chromatography (GPC)

Table 4.25 Degree of Polymerization for Poly(2-ethylhexyl methacrylate) samples from Dilute Solution Viscometry

[CCTA] $x10^6$ $molL^{-1}$	M_v	DP	1/DP $x\ 10^3$	$[1/DP-1/DP_o]$ $x\ 10^3$	[S]/[EHMA] $x\ 10^7$
0.00	93,144	470	2.13	0.00	0.00
0.76	81,140	409	2.44	0.31	1.70
2.25	61,183	309	3.24	1.11	5.56
2.98	42,055	212	4.72	2.39	6.70
3.70	37,527	189	5.28	3.15	8.31

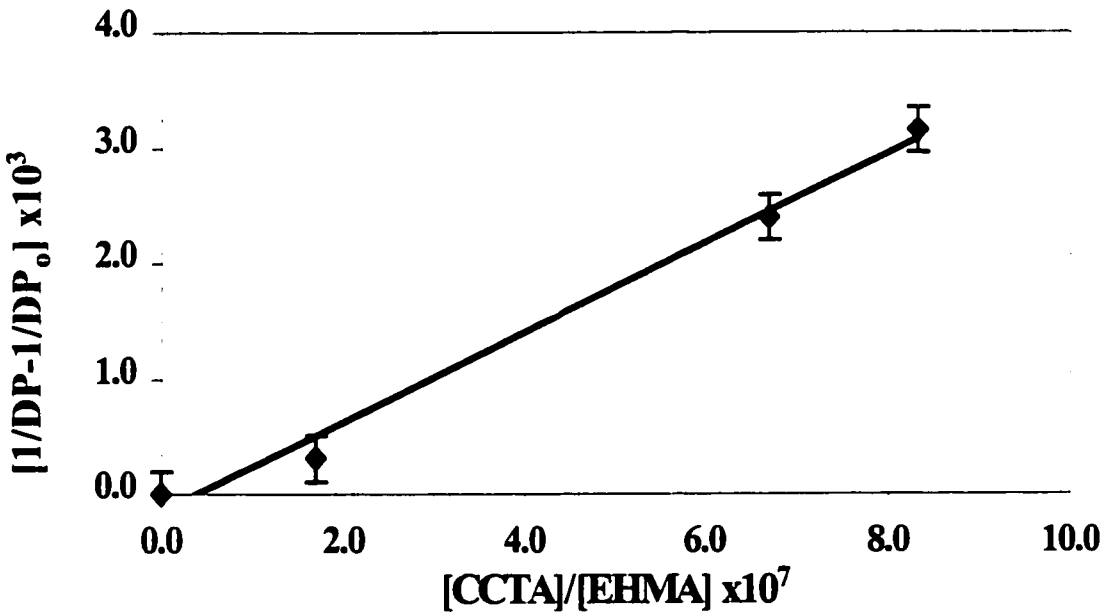


Figure 4.21 Mayo (regression) Plot for the Determination of Cs Value Poly(2-ethylhexyl methacrylate) samples Gel Permeation Chromatography (GPC)

Table 4.26 Catalytic Chain Transfer Constant (C_S) Values from Gel Permeation Chromatography (GPC)

Monomer	C_S Value
Methyl methacrylate	81,258
Butyl methacrylate	18,532
Styrene	1,035
2-Ethylhexyl methacrylate	3886

4.7 Polydispersity Index (PDI)

Polydispersity is simply the ratio of the weight average molecular weight M_w, to the number average molecular weight M_n, of a polymer sample. PDI is always greater thatn one for synthetic polymers. Free radical technique is known to yield samples with average polydispersity index of 2.0.

The polydispersity of the polymer samples prepared in this study were found to vary over the range 1.50 – 2.0, with poly (methyl methacrylate) samples having the highest values as shown in Table 4.27. These values are within the range reported for the same polymer with cobalt dimethylglyoxime as CCTA in bulk at 60°C [3, 43]. However, values lower than 2.0 in emulsion [9] and as high as 4.0 in bulk [46] have also been reported. It is apparent from this that different workers have quoted different values for the same system under the same experimental conditions. This shows that C_S values are not reproducible. The method of molecular weight analysis certainly has some influence on the C_S value obtained.

Literature values for polystyrene samples prepared in bulk are similar to those obtained with the samples studied. C_S values obtained for polystyrene were in the range of 1.3 –2.6. There are no literature reports for the other systems, therefore, no comparison can be made. Poly(butyl methacrylate) gave PDI values similar to those of poly(methyl methacrylate). However, the narrowest range was recorded for poly(2-ehtylhexyl methacrylate, with all values lying between 1.55 –

1.84. The PDI however, did not show any consistent trend with change in CCTA concentration.

Table 4.27 Effect of CCTA Concentration on Sample Polydispersity (PDI)

	PMMA		PBMA		PEHMA		Polystyrene	
Sample Number	[CCTA] x10^6 M	PDI	[CCTA] x10^6 M	PDI	[CCTA] x10^6 M	PDI	[CCTA] x10^6 M	PDI
Control	0.00	2.34	0.00	1.54	0.00	1.84	0.00	1.36
1	0.51	2.47	0.76	1.58	0.76	1.55	3.75	1.58
2	1.08	2.02	1.51	-	2.25	1.53	7.35	1.71
3	1.88	3.02	2.25	1.99	2.98	1.71	14.10	2.61
4	4.41	1.83	2.98	1.82	3.70	1.75	17.40	2.02

4.8 Conclusions

1. The BF_2-bridged cobalt alphafurildioxime $Co(\alpha\text{-fdo})_2(BF_2)_2 \bullet 2H_2O$ was successfully synthesized and characterized.

2. The catalytic chain transfer potential of the complex was investigated in the homo- and co-polymerization of some methacrylate and styrene monomers.

3. The molecular weights of all polymer samples studied were found to decrease upon addition of parts per million amounts of the complex (CTA).

4. The decrease in molecular weight of the polymer samples was observed to level off at higher concentrations of the CCTA.

5. C_S values obtained for methyl methacrylate, butyl methacrylate and styrene fell within the range reported in the literature for the systems.

6. The CCTA showed a higher chain transfer activity with the methacrylates than with styrene. This was attributed to the absence of an alpha methyl substituent in styrene and steric hindrance.

7. The presence of the CCTA did not affect the polydispersity index of the samples to any significant degree. This can be seen by the small difference between the PDI of the control sample and the sample with the highest concentration of the CCTA.

8. The effect of the CCTA on butyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and styrene oxide could not be established,

because the polymer samples could not be analyzed, or no polymer was formed (in case of styrene oxide).

9. The per cent conversion in the homopolymer systems was found to decrease with increasing concentration of the CCTA, while in the copolymer systems, the trend was non-uniform.

4.9 Recommendation for Further Study

As has been mentioned in this report, so far, all the efficient CCTAs reported in the literature have cobalt as the central metal atom. The most common oxidation state of the cobalt atom is +2. However, report on the use of cobalt (III) is available in the literature. Several factors can be manipulated to obtain a large array of high efficiency CCTAs.

Changing the central metal atom could lead to an entirely new category of CCTAs. However, since there is a prerequisite for possession of an unpaired electron, there exist a limit in this regard. One potential candidate is rhodium. Rhodium being in the same class as cobalt, and having been known to form chelate complexes similar to those of cobalt [46], may prove to be a viable option in the attempt to expand the collection of this class of highly efficient CCTAs.

In addition to changing the central metal atom, there are several kinds of ligands that would form stable chelate complexes with varying degree of solubility in various monomers. In this regard, two options are open: either the

subatituent on the ligand is changed, as has been seen in the literature, or the entire ligand is replaced with another that have suitable features that would allow cyclization by a bridging group.

A third option is to change the bridging group itself. Literature reports have shown that hydrocarbons can be used as bridging group depending on the functionality on the chelating ligand. It should however be noted that the linkage formed must be able to withstand the effect of temperature, oxidation and hydrolysis. These factors are bound to affect the integrity (cyclic and planar nature) of the complex thereby reducing or completely destroying its catalytic chain transfer ability.

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APPENDIX

APPENDIX A

Table A1 Monomer Chain Transfer Constants at 60°C

Monomer	$C_M \times 10^4$
Methyl methacrylate	0.07-0.25
Styrene	0.30-0.60
Vinyl chloride	10.8-16.0
Vinyl acetate	1.75-2.80
Acrylamide	0.6, 0.12[b]
Acrylonitrile	0.26-0.30
Ethylene	0.40-4.20
Methyl acrylate	0.036-0.325

[b] Value at 40°C

Table A2 Initiator Chain Transfer Constants at 60°C [16]

Chain Transfer Agent	C_I for Polymerization of	
	Methyl methacrylate	Styrene
2,2′-Azobisisobutyronitrile	0.02	0.091-0.14
Benzoyl peroxide	0.02	0.048-0.10
Cumyl hydroperoxide	0.33	0.063
Lauroyl peroxide	-	0.024
Cumyl peroxide	-	0.01
t-Butyl hydroperoxide	-	0.035
t-Butyl peroxide	-	0.00076-0.00092

Table A3 Mark-Houwink Constants for Some Polymer-Solvent pairs at 25°C [52-53]

Polymer	K value ($x10^{-5}$ dL/g)	α- value	Solvent
Poly(methyl methacrylate)	4.8	0.8	Chloroform
Poly(butyl methacrylate)	4.37	0.8	Chloroform
Polystyrene	7.16	0.76	Chloroform
Poly(2-ethylhexyl methacrylate)	-	-	-
[a]Methyl methacrylate-co-Butyl methacrylate	4.8	0.8	Butanone
Styrene-co-Methyl methacrylate	15.4	0.675	Butanone
Styrene-co-Butyl methacrylate	4.9	0.77	Butanone
Poly(butyl acrylate	6.85	0.75	Acetone

[a] values are for poly (methyl methacrylate) homopolymer

Table A4. Polymerization of MMA using AIBN and $[Co(dmg\text{-}2H)_2(BF_2)_2]$ as CCTA.

Time = 90 minutes

Temperature = 60°C

[AIBN] = 2.17×10^{-3} M.

S/#.	[CCTA]/[MMA] X10^4	$\eta_{int.}$	$M_V \times 10^{-5}$	1/DP	[1/DP-1/DPo]	% conv
Control	0.480	2.580	7.570	0.0132	0.0000	4.600
1	0.950	2.380	6.870	0.0146	0.0014	5.100
2	1.910	2.250	6.430	0.0155	0.0023	4.700
3	2.390	2.200	6.260	0.0160	0.0028	5.000
4	4.430	2.180	6.180	0.0162	0.0030	4.800
5	8.980	2.100	5.900	0.0169	0.0037	4.400
6	13.470	1.770	4.810	0.0208	0.0076	4.300
7	18.980	1.580	4.200	0.0238	0.0106	4.100

M_V = Viscosity average molecular weight of poly(methyl methacrylate)

$\eta_{intr.}$ = Intrinsic Viscosity

IMAGE EVALUATION
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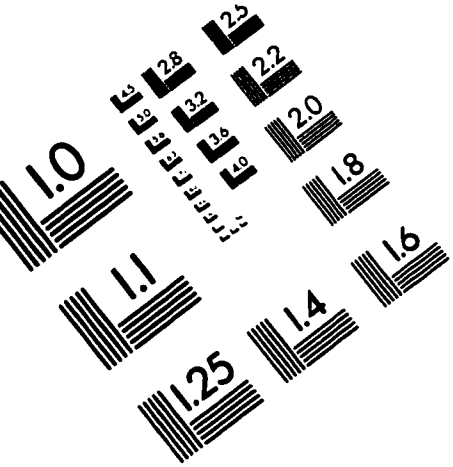

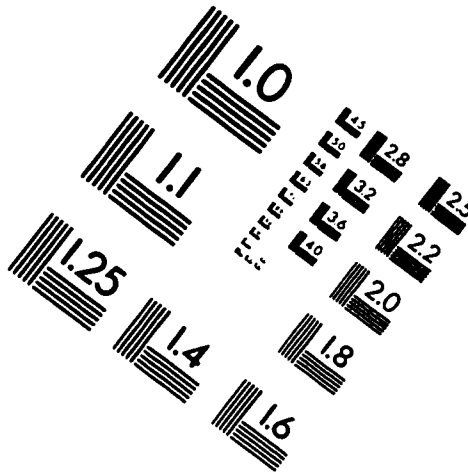

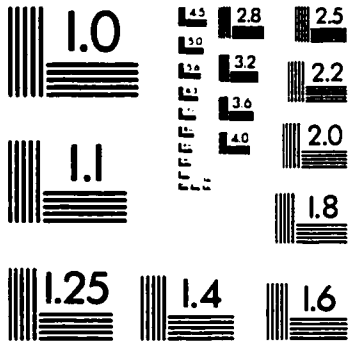

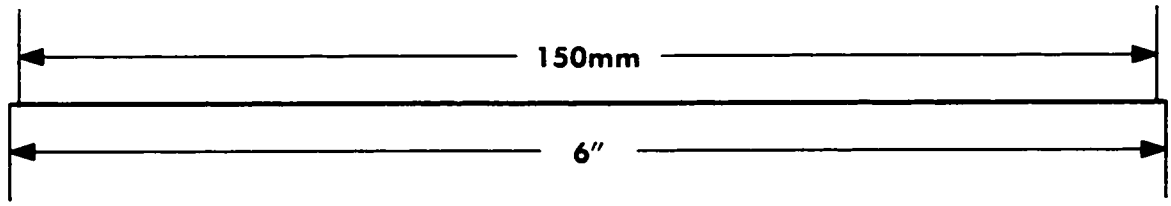

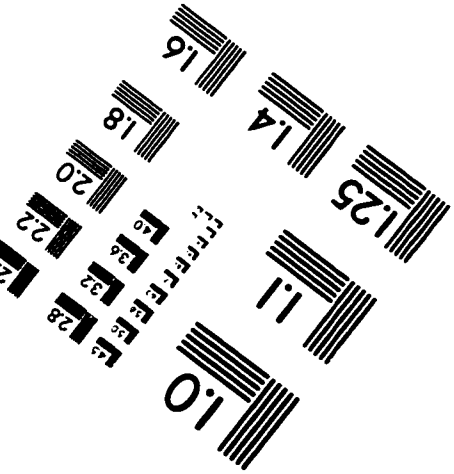

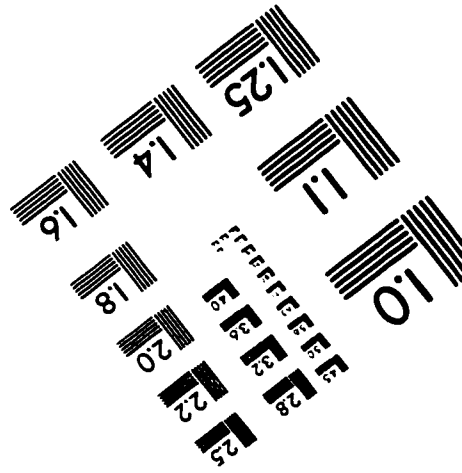

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